

***IN THE UNITED STATES PATENT AND TRADEMARK OFFICE***

Applicants: JANSSEN *et al.*

Title: PREPARATION OF SUPRAMOLECULAR POLYMERS CONTAINING  
QUADRUPLE HYDROGEN BONDING UNITS IN THE POLYMER  
BACKBONE

Appl. No.: 10/577,946

Int'l Filing  
Date: 11/4/2003

371(c) Date: 08/25/06

Examiner: Duc TRUONG

Art Unit: 1796

Conf. No.: 5217

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09/20/10

AMENDMENT UNDER 37 CFR 1.312

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Sir:

Applicants acknowledge, with appreciation, receipt of a Notice of Allowance date 16 July 2010 in the above-captioned application. In the course of auditing the prosecution record, Applicants noticed that three references, identified as "A5"- "A7" in an Information Disclosure Statement dated 03 May 2006, were not considered. No explanation was given. *See* Office Action dated 11 January 2010.

Applicants hereby respectfully request that the references be considered by the Examiner and be made of record. As a courtesy to the Examiner, the three documents are being resubmitted on Form PTO/SB/08, so that the Examiner may simply initial and sign the form

upon due consideration of the references. As well, copies of the listed documents are being provided for the Examiner's convenience. Because an English translation of reference A6 is not readily available, an English abstract of the publication is provided. The absence of an English translation of the entire documents does not, however, relieve the PTO from its duty to consider the document in its entirety. 37 CFR § 1.98 and MPEP § 609.

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<b>INFORMATION DISCLOSURE STATEMENT BY APPLICANT</b>  Date Submitted: May 3, 2006  (use as many sheets as necessary)			<b>Application Number</b>	10/577,946	
			<b>Filing Date</b>	May 3, 2006	
			<b>First Named Inventor</b>	Hendricus Marie Jassen	
			<b>Group Art Unit</b>	1796	
			<b>Examiner Name</b>	Duc Troung	
<b>Attorney Docket Number</b>	069818-3000				
Sheet	1	of	1		

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	A5	BRUNSVELD L ET AL., "Supramolecular Polymers", Chemical Reviews, vol. 1, Pages 4071-4097, XP002267453, December 2001.	
	A6	KATO T., "Supramolecular liquid crystal polymers. Formation of Molecular Self-Organized Structures and Their Functionalization", Kobunshi Ronbunshu (Japanese Polymer Science and Technology, pp. 855-862, English abstract on page 862, (1997)	
	A7	EL-GHAYOURY A ET AL., "Supramolecular Hydrogen-bonded oligo(p-phenylene vinylene) Polymers", Angewandte Chemi, Wiley-Vch, Weinheim, DE, vol. 40, no. 19, pages 3660-3663. XP002260390 (2001)	

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## Supramolecular Polymers

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Received April 23, 2001

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## I. Introduction

With the introduction of supramolecular polymers, which are polymers based on monomeric units held together with directional and reversible secondary interactions, the playground for polymer scientists has broadened and is not restricted to macromolecular species, in which the repetition of monomeric units is mainly governed by covalent bonding. The importance of supramolecular interactions within polymer science is beyond discussion and dates back to the first synthesis of synthetic polymers; the

materials properties of, e.g., nylons, are mainly the result of cooperative hydrogen bonding. More recently, many exciting examples of programmed structure formation of polymeric architectures based on the combination of a variety of secondary supramolecular interactions have been disclosed.

When the covalent bonds that hold together the monomeric units in a macromolecule are replaced by highly directional noncovalent interactions (Figure 1), supramolecular polymers are obtained. In recent years, a large number of concepts have been disclosed that make use of these noncovalent interactions. Although most of the structures disclosed keep their polymeric properties in solution, it was only after the careful design of multiple-hydrogen-bonded supramolecular polymers that systems were obtained that show true polymer materials properties, both in solution and in the solid state. Polymers based on this concept hold promise as a unique class of novel materials because they combine many of the attractive features of conventional polymers with properties that result from the reversibility of the bonds between monomeric units. Architectural and dynamic parameters that determine polymer properties, such as degree of polymerization, lifetime of the chain, and its conformation, are a function of the strength of the noncovalent interaction, which can reversibly be adjusted. This results in materials that are able to respond to external stimuli in a way that is not possible for traditional macromolecules. These aspects of supramolecular polymers have led to a recent surge in attention for this promising class of compounds<sup>1-3</sup> and have stimulated us to bring together materials science and supramolecular chemistry.<sup>4</sup> On the other hand, it is obvious that a large number of important properties of polymers require the covalent and irreversible bonding of the repeating units in the main chain. For applications in which all of these properties are important, supramolecular polymers are not the perfect choice. However, the opportunity to combine macromolecules and concepts derived from supramolecular polymers also has an enormous potential to alter the properties of polymers in a controlled way.

## II. The Term Supramolecular Polymers

Interest in supramolecular polymers has been stimulated to a great extent by the impressive progress made in supramolecular chemistry in general,<sup>5-8</sup> and in the field of synthetic self-assembling molecules in particular. The field in which



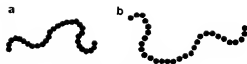
Luc Brunsveld (second from right) received his Ph.D. in Supramolecular Chemistry at the Eindhoven University of Technology in 2001 with professor E. W. Meijer. The Ph.D. research was focused on supramolecular architectures in water and a small part of that has been performed in the group of professor J. S. Moore at the University of Illinois, Urbana-Champaign. He did his undergraduate research in the group of professor E. W. Meijer on supramolecular hydrogen bonded polymers. His research interests are in the field of supramolecular architectures and chirality. Currently he is working as a postdoctoral fellow in the group of professor Walkmann at the MPI in Dortmund, Germany.

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Rint P. Sijbesma (left) did his graduate research with professor Roeland Nolte at the University of Nijmegen; the focus was on synthetic receptor molecules. From 1992 to 1993 he worked as a postdoctoral research assistant with professor Fred Wudl (University of California, Santa Barbara) on the synthesis of water-soluble  $C_{60}$ -derivatives. In 1993 he took his present position as assistant professor in the laboratories of professor E. W. Meijer, where he is working in the field of supramolecular polymer chemistry.

supramolecular chemistry and polymer science meet has developed into a vast area of research, ranging from the study of interacting biomacromolecules, such as DNA and proteins, to the self-assembly of large synthetic molecules into well-defined architectures. Examples of the latter include the formation of PMMA stereocomplexes, highly organized block-copolymer architectures, and self-assembled polymer architectures inspired by the structure of tobacco mosaic virus (TMV).<sup>9</sup> Noncovalent interactions have also been employed to fold macromolecules (aptly

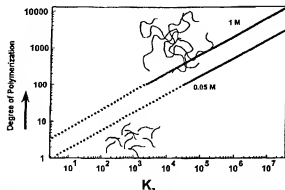


**Figure 1.** Schematic representation of a covalent polymer (a); and a supramolecular polymer (b).

named "foldamers")<sup>10</sup> into well-defined conformations. These examples of using secondary interactions in and between synthetic macromolecules typify the potential of a supramolecular approach to highly organized, functional materials.

Partly influenced by our own research interests, the focus in this review is on the role of specific, noncovalent interactions such as hydrogen bonding, metal coordination, and  $\pi$ - $\pi$  (or arene-arene) interactions to form so-called supramolecular polymers. The high directionality of these interactions inherently stresses the one-dimensional nature of these polymers. It is instructive to notice that from this point of view, supramolecular polymers and crystalline compounds are at opposite ends of the spectrum of molecular materials. In molecular crystals, it is difficult to define a dominant direction of the interactions - crystals are fundamentally 3-dimensional - and even when interactions are stronger in one direction than in others, all specific aggregation is lost when these materials are heated or dissolved. Supramolecular polymers, on the other hand, are 1-dimensional in nature, and in melts or (dilute) solutions of these materials distinguishable polymeric entities continue to exist. A fascinating intermediate class of materials consists of compounds that form polymers in the liquid crystalline state. Here, cooperativity between a relatively weak secondary interaction and excluded volume interactions (which are entropic in nature) leads to a significant degree of polymerization.<sup>11</sup> However, in the isotropic melt or in solution, most of the polymeric properties are lost. Because hydrogen-bonded liquid crystals have played an important role in developing the concept of supramolecular polymers, they will be covered in some detail in this review. Polymers that are held together by topological constraints, such as polycatenanes and polyrotaxanes, will not be treated in this review.<sup>12</sup>

Taking everything into account, we like to propose the following definition for supramolecular polymers: *Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.* In the past the term "living polymers" has been used for this type of polymers. However, to exclude confusion with the important field of living polymerizations, we prefer to use the term supramolecular polymers. With this definition, the term supramolecular polymer is rather restricted and not



**Figure 2.** Theoretical relationship between the association constant  $K_a$  and DP, using a simple isodesmic association function, or "multistage open association" model.

used for telechelic macromolecules reversibly bound together by specific supramolecular interactions. However, modified telechelics are included in this review because many issues in the field are important for associating telechelics as well.

### III. General Aspects of Supramolecular Polymers

It is useful to review some of the general aspects of the supramolecular approach, taking into account the limitations of our definition of supramolecular polymers. Using a directional complementary couple (A–B) or a self-complementary unit (A–A), it is possible to form all known structures of polymers, including linear homo- and copolymers, cross-linked networks, and even (hyper)branched structures in the case of complementary couples.<sup>13</sup> In supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction.<sup>14</sup> The degree of polymerization is obviously dependent on the concentration of the solution and the association constant, and a theoretical relationship is given in Figure 2.

To obtain polymers with a high molecular weight, a high association constant between the repeating units is a prerequisite. In analogy with covalent condensation polymers, the chain length of supramolecular polymers can be tuned by the addition of monofunctional "chain stoppers".<sup>15</sup> This also implies that impurities will have a strong influence on the maximal DP, because it is easy to have a small fraction of monofunctional impurity in the synthesis of the bifunctional monomer. Hence, as in traditional polymer synthesis, the purification of the monomers is extremely important to obtain high molecular weights.

In another approach, supramolecular polymers can be formed by planar structures that have the possibility to assemble on both sides of the plane. Here, one structural element is responsible for the formation of the polymer, and chain stoppers are difficult to design. Hence, the DP is completely governed by the association constant and the concentration. As a result of the structural motive, these supramolecular polymers are rather stiff and resemble rodlike poly-

mers, with interesting architectural properties but without significant materials properties in the bulk.

In a third approach, supramolecular polymers are based on the reversibility of metal-coordination bonding. These polymers are the closest analogues to conventional macromolecules, because most of the polymers disclosed make use of strong bonding,<sup>16</sup> in which the reversibility can be tuned by chemical means only. However, appropriate choice of the metal ion can give rise to bonding that resembles that of the other two approaches. The DP of the polymers in the case of the coordination polymers is similar to that of the condensation polymers, and achieving exact stoichiometry is of distinct importance here.

True supramolecular polymers are reversible aggregates that can break and recombine on experimental time scales. It is this feature that has been investigated in detail by Cates in a physical model, predicting stress relaxation and other viscoelastic properties of entangled "living polymers" as a function of the interaction strength of the monomer and groups.<sup>17–19</sup> Although this model was made for cylindrical micelles, it is shown by the work on ureidopyrimidone-based supramolecular polymers that the model also describes in detail the viscosity behavior of reversible supramolecular polymers. Many of the materials properties of supramolecular polymers are those well-known for traditional polymers, although the reversibility will lead to an unconventional temperature dependence of the materials' properties.

### IV. Supramolecular Polymers Based on Hydrogen Bonding

Although hydrogen bonds between neutral organic molecules are not among the strongest noncovalent interactions, they hold a prominent place in supramolecular chemistry because of their directionality and versatility.<sup>20–22</sup> The relationship between the degree of polymerization and the strength of the noncovalent interaction between monomers in a supramolecular polymer (see Figure 2) implies that cooperativity is required to obtain significant degrees of polymerization. Hence, either multiple-hydrogen bonds must be used or hydrogen bonds should be supported by additional forces, like excluded volume interactions. Examples of both approaches to hydrogen-bonded supramolecular polymers will be discussed.<sup>23</sup>

#### A. Strength of Hydrogen Bonds

Combining several hydrogen bonds in a functional unit is a valuable tool for increasing the strength of this interaction, and employing a particular arrangement of the hydrogen bonding sites enhances its specificity. The strength of single hydrogen bonds basically depends on the nature of donor and acceptor, although it is influenced to a large extent by the solvent. Association strength between multiple hydrogen-bonding units obviously depends on the same factors, as well as on the number of hydrogen bonds. It has also been shown that the particular arrange-

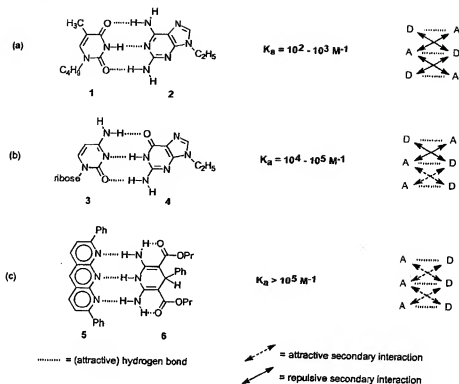


Figure 3. Stability of complexes with different hydrogen-bonding motifs.

ment of neighboring donor and acceptor sites is an additional factor which significantly affects the strength of the complexation. This phenomenon was first recognized for the association of linear arrays of 3 hydrogen-bonding sites (Figure 3); whereas complexes between the common ADA-DAD (1-2) motif exhibit an association constant of around  $10^2 \text{ M}^{-1}$  in chloroform, this value is around  $10^4 \text{ M}^{-1}$  in complexes with a DAA-DDA (3-4) motif, while AAA and DDD arrays (5-6) exhibit association constants exceeding  $10^5 \text{ M}^{-1}$ . Detailed calculations by Jorgensen<sup>24,25</sup> showed that this effect is due to differences in secondary interactions between these motifs. In the complexes, diagonally opposed sites repel each other electrostatically when they are of the same kind (both donor or both acceptor), whereas disparate sites attract each other. In the DDD-AAA motif the number of attractive secondary interactions is maximized, and in the ADA-DAD motif the number of repulsive interactions is at its largest.

Very stable complexes can be obtained when quadruple hydrogen-bonding units are employed.<sup>26-30</sup> Aspects of multiple hydrogen-bonding units that are of special importance with respect to application in supramolecular polymers are the self-complementarity of DADA and DDAA arrays and the possibility of tautomerism. The latter may lead to loss of complexation when complementarity is lost, or when a DDAA array tautomerizes to a DADA array with a higher number of repulsive secondary interactions. We have reported on self-complementary quadruple H-bonding units based on mono-ureido derivatives of diamino-triazines<sup>29</sup> (DADA-array) with a dimerization constant of  $K_{\text{dim}} = 2 \times 10^4 \text{ M}^{-1}$  and hydrogen-

bonding units based on 2-ureido-4[1H]-pyrimidinones (DDAA), which dimerize in chloroform with an association constant of  $K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$ .<sup>30,31</sup> The supramolecular polymers that were developed using these hydrogen-bonding units will be discussed in detail below. Zimmermann and co-workers have reported a very stable self-complementary quadruple hydrogen-bonding unit (7), depicted in Figure 4, in which all tautomers can dimerize via quadruple hydrogen bonds.

There is ample opportunity for developing new multiple hydrogen-bonding units for use in supramolecular polymers with novel, attractive features, such as ease of synthesis, insensitivity to tautomerization,<sup>28</sup> and stronger association by using arrays of 6 bonds<sup>32</sup> or 8 hydrogen bonds.<sup>33</sup> The use of heteroaromatic compounds as multiple hydrogen-bonding units for self-assembly has recently been reviewed.<sup>34</sup>

Application of hydrogen-bonding units as associating end-groups in difunctional or multifunctional molecules results in the formation of supramolecular polymers with varying degrees of polymerization (DP). The early examples of hydrogen-bonded supramolecular polymers rely on units, which associate using single, double, or triple hydrogen bonds that all have association constants below  $10^3 \text{ M}^{-1}$ . In isotropic solution, the DP of these polymers is expected to be low. In the liquid crystalline state, however, the interactions are stabilized by excluded volume interactions, and the DP is much higher. Examples of linear supramolecular polymers based on weak hydrogen-bonding interactions assisted by liquid crystallinity or phase separation will be treated below, followed by a discussion of supramolecular

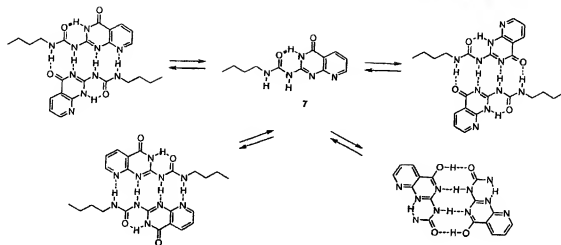


Figure 4. Hydrogen-bonding unit 7 that dimerizes via quadruple hydrogen bonding without regard to tautomeric form.

polymers based on strong hydrogen-bond interactions that persist in the isotropic state (melt or solution).

## B. Hydrogen Bonding Enforced by Liquid Crystallinity

The first hydrogen-bonded supramolecular polymers all showed liquid crystallinity, although the separate components making up these polymers displayed a narrow liquid crystalline regime or no liquid crystallinity at all. The liquid crystalline phase in the supramolecular polymer is stabilized by the increased aspect ratio of aggregates compared to the constituent molecules. There is a strong cooperativity between association and the induction of the liquid crystalline phase, because anisotropy in the liquid crystal strongly enhances the degree of polymerization of the hydrogen-bonded molecules.<sup>35</sup> Liquid crystalline supramolecular polymers are unique in the respect that they combine the potential to exhibit the electrooptical properties associated with low-molar-mass liquid crystals with the benefit of the good mechanical properties of conventional polymers.<sup>36</sup> Odijk,<sup>37,38</sup> van der Schoot,<sup>39</sup> and Ciferri<sup>40</sup> developed a theoretical basis for the relation between chain growth and orientation in supramolecular liquid crystals.

The group of Lehn is recognized to be the first to develop a supramolecular main-chain polymer. By triple hydrogen bonding between difunctional diaminopyridines (**8**) and difunctional uracil (**9**) derivatives (Figure 5) supramolecular polymer chains were formed (**10**).<sup>41,42</sup> The 1:1 mixture of **8** and **9** exhibits liquid crystallinity over a broad temperature window, whereas, in contrast, the pure compounds are solids which melt in an isotropic liquid without displaying a liquid crystalline phase. Because of the chirality of the tartaric acid spacer used, the fibers observed by electron microscopy showed biased helicity.<sup>43</sup> Lehn and co-workers expanded the scope of supramolecular polymers by the development of rigid rod polymers (**11**, Figure 5).<sup>44,45</sup> In these polymers, a rigid 9,10-dialkoxyanthracene core connects the hydrogen-

bonded groups via an imide group. Because of the increased molecular rigidity, the system is not thermotropic liquid crystalline, but a lyotropic liquid crystalline phase is observed in apolar solvents, that is birefringent and highly viscous.

A number of supramolecular liquid crystalline polymers based on a single hydrogen bond have been reported. Incorporation of single hydrogen-bonding units is synthetically more straightforward than those with triple hydrogen bonds, and, particularly, the single hydrogen bond between a pyridyl unit and carboxylic acids has been utilized frequently in supramolecular liquid crystalline polymers (LCPs).<sup>46–50</sup> The complexation between a pyridyl unit and a carboxylic acid is stronger than carboxylic acid dimerization; a  $K_a$  value of approximately 500 M<sup>-1</sup> was estimated for the pyridyl/carboxylic acid complex.<sup>47</sup> Kato and Fréchet have described a variety of self-assembled side-chain liquid crystalline polymers (SLCPs), with various backbones.<sup>48,49</sup> Polyacrylates and polysiloxanes functionalized with pendant benzoic acids display stable mesophases upon self-assembly with stilbazoles. The reverse principle has been employed for the formation of supramolecular liquid crystalline polyurethanes.<sup>50</sup> Furthermore, the stability of the induced mesophase has been enlarged by employing the double hydrogen bond between benzoic acids in the polymer main-chain and 2-(acylamino)pyridines.<sup>51,52</sup>

Utilization of the single hydrogen bond between pyridine and benzoic acids in SLCPs has been a source of inspiration for other groups in the development of main-chain supramolecular polymers based on diacids and dipyridines.<sup>53–56</sup> Supramolecular rod-coil polymers have been developed by assembly of 4,4'-bipyridines and telechelic polypropylene oxide with benzoic acid end-groups, which show highly ordered liquid crystalline phases.<sup>57</sup> The use of tartaric acid derivatives in combination with bipyridine units resulted in the formation of hydrogen-bonded, chiral main-chain LCPs, as has been shown by circular dichroism measurements, optical microscopy, and X-ray data.<sup>58,59</sup>



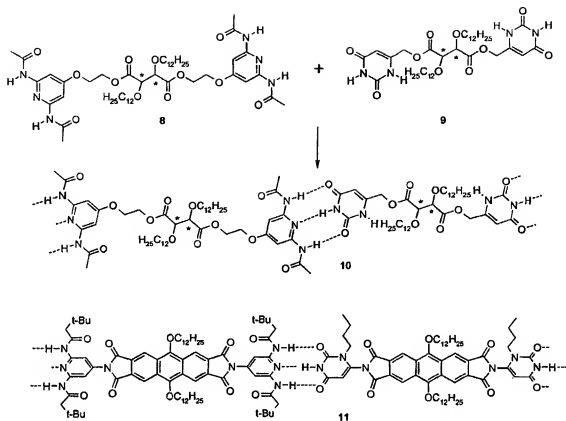


Figure 5. Liquid crystalline supramolecular polymers developed by Lehn, based on triple hydrogen bonds: from chiral, tartaric acid based monomers (10) and from rigid monomers (11).

A columnar mesophase has been used by the group of Percec for the creation of hydrogen-bonded supramolecular polymers.<sup>60,61</sup> The phase separation of the apolar side groups of substituted benzamides with the core of the molecule accounts for the self-assembly into a cylindrical structure in which hydrogen bonding acting along the columnar axis occurs and stabilizes the column.

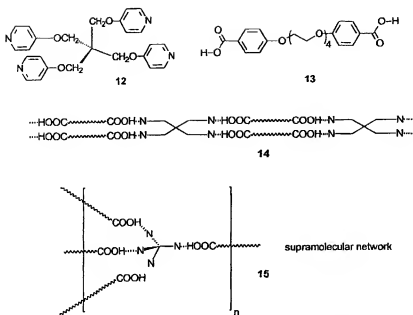
Next to side-chain LCPs and main-chain LCPs, supramolecular networks were obtained by complexation of bipyridines with polyacrylates containing pendant benzoic acid groups. In a related approach, Kato and Fréchet have studied supramolecular networks based on low-molecular-weight components, in which a trifunctional benzoic acid derivative was combined with a difunctional pyridine derivative.<sup>62</sup> The hierarchy of the LC-phase that was formed turned out to be dependent on the flexibility of the trifunctional compound used.

Although chain extension based on single hydrogen bonding is observed, supramolecular materials based on this interaction, in most aspects, resemble small molecules more than they resemble polymers. Only the triple hydrogen-bonded supramolecular polymers reported by Lehn show some typical polymer properties, such as the ability to draw fibers from the melt. By using multifunctional low-molecular-weight building blocks, Griffin was able to obtain materials that exhibited polymer-like properties.<sup>63</sup>

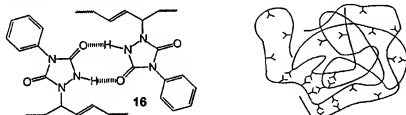
Hydrogen bonding between pyridine units in a tetrafunctional compound (12) and benzoic acid units in difunctional compounds (13, Figure 6), resulted in the formation of reversible ladder-like polymers (14) or networks (15). These materials are liquid crystalline, and the large drop in material properties above the isotropisation temperature demonstrates that, also here, the interplay between association and liquid crystallinity is instrumental in the process of polymerization.<sup>63</sup> DSC studies on these networks reveal a memory effect, resulting in a consistent decrease of crystallinity as the time the material is in the isotropic state increases.<sup>64</sup>

### C. Hydrogen Bonding Enforced by Phase Separation

The methodology of increasing the strength of a relatively weak hydrogen-bond interaction by (crystalline) domain formation is frequently encountered in chain extension of conventional polymers, and is in principle analogous to the enforcement of association in the liquid crystalline phase. Lillia et al. has shown that by end-capping of poly-THF with benzoic acid functionalities, the material properties improve significantly due to the formation of large crystalline domains of the hydrogen-bonded units.<sup>65</sup> Furthermore, end capping of poly(dimethylsiloxane) with benzoic acid groups has been reported to result in a change in polymer properties upon functionalization. However, the change in properties seems to be less



**Figure 6.** Formation of a linear ladder-type supramolecular polymer (14) or a hydrogen-bonded network (15) based on the single hydrogen bond between a pyridine unit and a benzoic acid unit.



**Figure 7.** Formation of a supramolecular network by hydrogen bonding between phenylurazole units and subsequent formation of ordered clusters.

remarkable than the results obtained with poly-THF.<sup>66</sup> On the basis of detailed FTIR spectroscopy and viscosimetry studies, a quantitative model for the chain length and weight distribution of the functionalized polysiloxane in solution was described by Bouteiller et al.<sup>67</sup> These associative polymers with hydrogen-bonded groups, either telechelic or in the side-chains, are of considerable interest for numerous applications, such as rheology modifiers, adhesives, adsorbents, coatings, surfactants, and stabilizers, because of the reversibility of interactions in the chain and between chains.<sup>68</sup> Particularly, Stadler made an impressive contribution to this field by studying the properties of polybutadienes functionalized with hydrogen-bonded phenylurazole units (16, Figure 7).<sup>69–87</sup>

Because of their reversible chain extension and the subsequent formation of small crystalline domains, the functionalized polymers exhibit properties typical for thermoplastic elastomers. At low temperatures the hydrogen-bond interaction contributes to the properties comparable to covalent interactions, whereas at high temperatures these interactions disappear and the materials exhibit flow behavior typical for a low-molecular-weight polymer. DSC,<sup>72,73</sup> light and X-ray scattering,<sup>71,74</sup> dynamical mechanical analy-

ses,<sup>75–81</sup> dielectric spectroscopy<sup>82,83</sup>, deuterium-NMR,<sup>84</sup> and IR spectroscopy<sup>85–87</sup> were used to analyze the properties of these materials.

Although the strength of association between units, which assemble by only a single or double hydrogen bond, is low, chain extension by these synthetically accessible units is a versatile tool for gaining a significant improvement in material properties. A modest degree of polymerization in combination with physical interchain interactions by means of domain formation results in high-molecular-weight assemblies with improved material properties. Without domain formation, or when low-molecular-weight building blocks are used, a very high degree of polymerization, and consequently a high association constant, is required, as will be discussed in the following section.

## D. Strong Dimerization of Multiple Hydrogen-Bonding Units

The number of supramolecular polymers based on very strong multiple hydrogen-bonded units is relatively small because of the increased synthetic efforts required for the synthesis of the monomers. Intriguing architectures such as nanotubes<sup>88</sup> are obtained

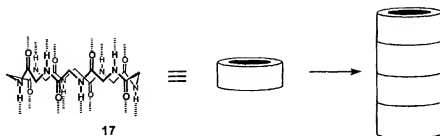


Figure 8. Formation of nanotubes based on hydrogen bonding between cyclic peptides.

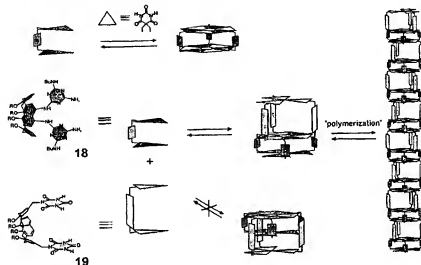


Figure 9. Nanorods based on the cyclic hydrogen-bonding motif of cyanuric acid and melamine in bifunctional calixarene derivatives 18 and 19. (Reprinted with permission from ref 106. Copyright 1999 American Chemical Society.)

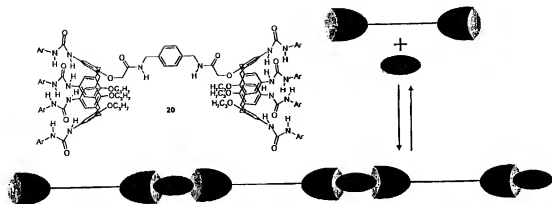
when bifunctional compounds with cyclic arrays of hydrogen-bonding sites are used. Ghadiri has studied nanotubes that self-assemble from cyclic peptides (17). These tubes can be considered reversible polymers because of their multiple-hydrogen bonding. On the basis of earlier work by De Santis<sup>98</sup> and Tomasic,<sup>90</sup> cyclic peptides were designed, composed of an even number of alternating *D*- and *L*-amino acids, which assemble into extended linear stacks through hydrogen bonding between the flat ring-shaped peptides (Figure 8).<sup>91–102</sup>

These nanotubes were found to be very robust and turned out to be stable to a wide range of pH and solvents, as well as to physical stress.<sup>94</sup> From variable temperature studies in chloroform, Ghadiri and co-workers concluded that the dimeric form was favored over the monomer by 23 kJ mol<sup>-1</sup>, and they postulated that this gain in stabilization energy would be additive as the number of assembled rings increased.<sup>95</sup> The association constant is dependent on the peptide residue used and is around 2500 M<sup>-1</sup>. By selective backbone *N*-methylation the self-assembly of the peptides is limited to the formation of dimers.<sup>96,97</sup> Subsequently linking of two of the *N*-methylated peptides by a short spacer results again in the formation of linear reversible polymers, this time with the direction of chain growth perpendicular to the direction of hydrogen bonding. A clever combination of this approach with the photoisomerization

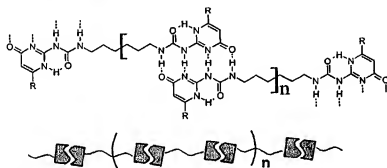
of an azobenzene unit, resulted in a system that can be switched between intramolecular dimerization and linear polymer formation by UV light.<sup>98,99</sup> The cyclic peptides were shown to self-assemble in membranes to form trans-membrane ion channels,<sup>100</sup> whose orientation in the membrane has been studied in detail with different IR techniques.<sup>101</sup> The nanotubes have been used in size-selective ion-sensing on self-assembled monolayers.<sup>102</sup> Tubular assemblies based on hydrogen bonding between cyclic  $\beta$ -peptides, have been reported by Seebach,<sup>103</sup> and by Ghadiri who showed that these related structures also self-assemble to form membrane-spanning ion channels.<sup>104</sup> Stable peptide nanotubes have been obtained by using the hydrogen-bond formation between urea groups in cysteine based macrocycles.<sup>105</sup>

The groups of Reinhoudt<sup>106</sup> and of Whitesides<sup>107</sup> have reported independently on the formation of supramolecular "nanorods" based on the well-known cyanuric acid–melamine motif. These hydrogen-bonded polymeric rods are composed of parallel cyanuric acid–melamine rosettes (Figure 9).

Both groups employed the same rationale: the self-assembly of dimelamine derivative with a dicyanurate derivative in which the spatial distance between the two cyanurate units is different from the distance between the two melamine units. It was anticipated that this mismatch prevented the formation of a closed disklike assembly and induced the formation



**Figure 10.** Bifunctional calixarene derivative **20** and a cartoon-like representation of its polymerization induced by small molecules.



**Figure 11.** Polymeric assembly of a bifunctional ureidopirimidinone derivative.

of polymeric entities. A 1:1 mixture of dimelamine (**18**) and dicyanurate (**19**) resulted in a viscous solution, indicating that high-molecular-weight aggregates were formed. The nature of the aggregates was further investigated by NMR spectroscopy, gel permeation chromatography (GPC), and transmission electron microscopy (TEM).

The group of Rebek Jr. has developed an ingenious way to form supramolecular polymers by utilizing the hydrogen bonding between urea functionalized calixarenes (Figure 10).<sup>109–112</sup> These calixarenes had been shown to form very stable dimeric capsules which bind a solvent molecule inside their cavity. Association of bifunctional molecules consisting of two covalently connected calixarene moieties (**20**) results in the formation of "polycaps". The association between the monomers is based upon hydrogen bonding in cooperation with complexation of a small guest; the polymerization of the assembly is driven by encapsulation of small guests such as benzene. Solutions of these molecules in *o*-dichlorobenzene show polymer-like rheological behavior, with a strong concentration-dependent viscosity.<sup>111</sup> The physical integrity of the noncovalent assemblies under shear was demonstrated by the observation of strong normal forces in rheometry experiments. The "polycaps" can be drawn into fibers with a tensile strength in the order of  $10^8$  Pa.<sup>109</sup> Networks from tetrafunctional molecules in solution display a stronger elastic component in their rheological behavior, and they have complicated time dependent properties such as shear thickening. When the "polycaps" are fitted with

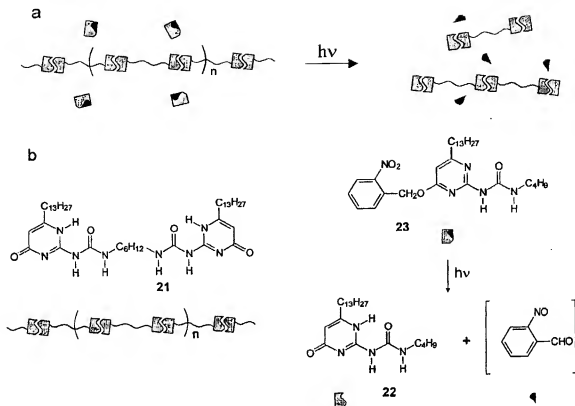
long alkyl chains, chloroform solutions develop liquid crystallinity.<sup>112</sup>

Although these supramolecular polymers possess intriguing new properties, synthetic barriers hamper extensive study of the mechanical properties of these materials. The supramolecular polymers discussed above are the products of multistep synthesis, and it is a daunting task to prepare sufficient amounts of material for evaluations such as melt-rheological experiments and tensile testing. The development of the ureidopirimidinone functionality, a synthetic very accessible quadruple hydrogen-bonding unit with a very high association constant, has helped enormously to open the way to complete exploration of all aspects of supramolecular polymers.

## E. Ureidopirimidinone-Based Polymers

The ureidopirimidinone unit can be made in a one-step procedure from commercially available compounds,<sup>29,31</sup> and it dimerizes with an association constant of  $6 \times 10^7 \text{ M}^{-1}$  in  $\text{CDCl}_3$ . Difunctional compounds (**21**), possessing two of these ureidopirimidinone units, form very stable and long polymer chains in solution as well as in the bulk (Figure 11).<sup>113,114</sup>

Dissolving a small amount of this low-molecular-weight compound (**21**) in chloroform results in a solution with a high viscosity. It can be calculated that polymers with chain lengths of the order of  $10^6$  Da can be formed when highly purified monomers are used. The presence of monofunctional impurities



**Figure 12.** Light-induced depolymerization of UPy-based supramolecular polymers. Concept (a); and compounds used (b).

is expected to lead to a dramatic reduction in DP, because they will act as "chain stoppers". In fact, deliberate addition of small amounts of monofunctional compounds (22) results in a sharp drop in viscosity, proving the reversibility and unidirectionality of association. The reversibility of the linkages between the building blocks is instrumental in the development of materials that change their properties in response to environmental changes, so-called 'smart materials'. Application of a light-sensitive monofunctional compound (23) yielded a material from which the degree of polymerization in solution could be tuned by UV irradiation (Figure 12).<sup>115</sup>

Although the supramolecular polymers based on bifunctional ureidopyrimidinone derivatives in many ways behave like conventional polymers, the strong temperature dependence of their mechanical properties really sets them apart from macromolecular polymers. At room temperature, the supramolecular polymers show polymer-like viscoelastic behavior in bulk and solution, whereas at elevated temperatures liquid-like properties are observed. These changes are due to a 3-fold effect of temperature on the reversible polymer chain. Because of the temperature dependence of the  $K_a$  value of UPy association, the average DP of the chains is drastically reduced at elevated temperatures. Simultaneously, faster dynamics of the scission–recombination process leads to faster stress relaxation in an entangled system. These two effects occur in addition to the temperature-dependent stress relaxation processes that are also operative in melts

or solutions of conventional polymers. Similar to the behavior in the melt, solution viscosities of UPy-based supramolecular polymers are also strongly temperature-dependent. Recently a very surprising inversion of the normal temperature-dependence of the solution viscosity was observed in solutions of preorganized difunctional compounds (24), which form a mixture of linear polymer chains and cyclic dimers (Figure 13).<sup>116</sup> The thermodynamic parameters of this equilibrium are such that polymerization is favored at higher temperatures. As a result, the viscosity of a 145 mM chloroform solution of the compound was observed to increase by a factor of 3.9 when the temperature was increased from 255 to 323 K. Entropy-driven polymerizations are rare, and the unexpected effect in this system is the first time it was observed in a reversible synthetic system.

The quadruple hydrogen-bonded unit has been further employed in the chain extension of telechelic polysiloxanes,<sup>117</sup> poly(ethylene/butylenes), polyethers, polyesters, and polycarbonates.<sup>118</sup> In these compounds, the material properties were shown to improve dramatically upon functionalization, and materials were obtained that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds. This strategy can be seen as closing the gap between polymers and oligomers by taking the best of both worlds. Especially in the field of conjugated polymers for plastic electronic devices, expectations for future applications of this strategy are high.<sup>119</sup>

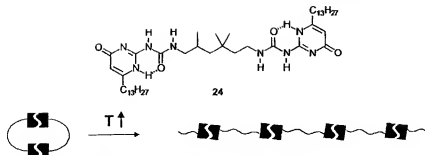


Figure 13. Entropy-driven ring-opening polymerization of the cyclic dimer of 24.

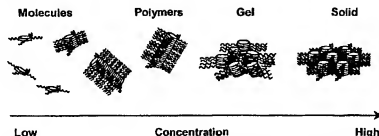


Figure 14. Self-assembly of discotic molecules with the different aggregates given as a function of concentration.

Very recently, Coates et al. used a vinyl-substituted Upy-unit to be part of an olefin polymerization using the Brookhart catalyst. With small amounts of Upy-units incorporated, the polyolefins showed thermo-plastic elastomeric properties.<sup>120</sup>

The reversibility of supramolecular polymers adds new aspects to many of the principles that are known from condensation polymerizations. A mixture of different supramolecular monomers, for example, will yield copolymers, but it is extremely simple to adjust the copolymer composition instantaneously by adding an additional monomer. Moreover, the use of monomers with a functionality of three or more, will give rise to a network formation. However, in contrast to condensation networks, the "self-healing" supramolecular network can reassemble to form the thermodynamically most favorable state, thus forming denser networks.<sup>121</sup>

Although the "virtual" molecular weight and lifetime of supramolecular polymers and networks based on strong hydrogen-bonding functionalities is extremely high, low creep resistance is an intrinsic property of these materials that may limit future applications. Strong interchain interactions, especially in crystalline domains, may be employed to tackle this problem and may lead to thermoplastic elastomers with enhanced processability. With the facile synthetic accessibility of these self-complementary Upy-units at hand it is expected that many novel materials properties can be obtained, and multiple hydrogen bonding between repeating units offers an ideal motive for supramolecular polymers, both in solution and in the solid state.

## V. Supramolecular Polymers Based on Discotic Molecules

Discotic molecules are ditopic structures with a disc-shaped core and a periphery of a number of

flexible side-chains. The core generally consists of a planar aromatic system, whereas the side-chains are usually flexible alkyl chains.<sup>122</sup> This anisotropy generates thermotropic liquid crystalline mesophases, as was first discovered in 1977. The structural properties make discotic molecules highly suitable for the formation of supramolecular polymers in solution. The strong  $\pi$ - $\pi$  (or arene-arene) interactions of their cores make discotics prone to aggregate in either polar or apolar solvents, forming rodlike or wormlike polymers. Because of the polarizability and good intermolecular contact of the planar aromatic system attractive intermolecular stacking interactions occur. In polar or in very apolar solvents the  $\pi$ - $\pi$  stacking may be strengthened significantly by solvophobic interactions. In this section we will use the general term arene-arene interactions, but it should be noted that solvophobic effects are generally stronger than  $\pi$ - $\pi$  stacking.

Actually, discotic liquid crystals are the only type of liquid crystals able to form linear architectures, i.e., supramolecular polymers, in dilute solution by means of these stacking interactions. Other types of liquid crystals have ordering interactions of the same order of magnitude in at least two dimensions. This gives rise to gels at appreciable concentration, i.e., uncontrolled growth of the aggregates, whereas at lower concentrations the intermolecular interactions are generally too weak to generate polymeric architectures.

In discotics, the interdisk stacking interaction is several orders of magnitude stronger than the inter-columnar interactions, because of the phase separation induced by the side-chains whose van der Waals interactions are much weaker. Generally, long polymers are obtained via discotics that have strong and specific intermolecular interactions, either via a large aromatic core or via additional specific intermolecular

interactions such as hydrogen bonding. Moreover, the combination of two or more interactions accounts for the formation of highly ordered columns. Only at higher concentrations, the intercolumnar interactions become prominent, and superstructure formation or gelation occurs followed by the liquid crystalline phase in the bulk. An illustrative picture displaying the self-assembly of discotic molecules into supramolecular polymers is given in Figure 14.

In this section we will discuss those discotic molecules that have been shown to form supramolecular polymers. For information concerning discotic liquid crystals in general, their synthesis, behavior, and applications the reader is referred to review the literature.<sup>122</sup> The mechanical properties of the supramolecular polymers from discotic liquid crystalline molecules are not particularly interesting and have not been studied in detail, therefore, these properties will not be covered here. It should be noted, however, that because of the strong intermolecular interactions, the thermotropic mesophases of discotics generally show much better mechanical properties than those of calamitics, illustrating the beneficial properties of strong unidirectional interactions. Because the specific interactions between the disks in the rigid-rod supramolecular polymers often gives rise to well-defined architectures, we will discuss the architectures of these supramolecular polymers in more detail.

This section is divided into three parts. The first part, section A, deals with rodlike polymers formed by the arene-arene interactions. In the second part (B) discotics will be discussed for which unidirectional hydrogen bonding is the driving force for supramolecular polymerization. Finally, section C will deal with supramolecular polymers formed by a combination of arene-arene interactions and hydrogen bonding.

## A. Arene-Arene Interactions

### 1. Triphenylenes

Alkoxy substituted triphenylenes (25a-e) were among the first discotic molecules shown to be liquid crystalline.<sup>123,124</sup> A large variety of different triphenylenes has been synthesized and their thermotropic mesomorphism has been studied in great detail.<sup>122</sup> The aromatic core of triphenylenes is relatively small; nevertheless, polymerization of triphenylenes (25a-c) does occur in deuterated hexadecane as shown with small angle neutron scattering (SANS).<sup>125</sup> At low concentrations the DP is small, but at higher concentrations ( $10^{-3}$  M) rodlike polymers are observed. The intercore distance was determined to be  $\sim 6$  Å, a value significantly larger than the stacking distance of  $\sim 3.5$  Å in the liquid crystalline state. This result indicates that the molecules are loosely stacked, most probably due to the absence of specific intermolecular interactions. Furthermore, the triphenylenes are highly mobile and undergo both lateral and rotational translation, similar to that in the liquid crystalline state.<sup>126</sup> The supramolecular polymerization of triphenylenes was also visualized using optical techniques. Increase of the concentration of a solution of

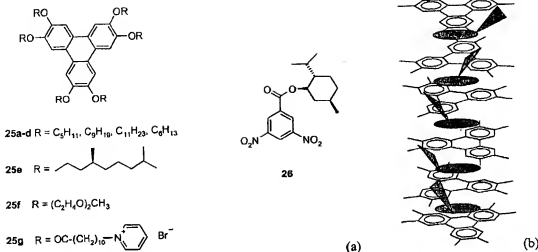
triphenylene 25d resulted in a broadening of the UV-Vis spectrum and an increase of the absorbance.<sup>127</sup>

Ringsdorf and co-workers have shown that triphenylenes can form alternating donor-acceptor supramolecular polymers in solution by doping them with equimolar amounts of electron acceptors.<sup>128,129</sup> Supramolecular polymers formed in this manner allow for electron transfer perpendicular to the molecular planes upon excitation of the chromophores, i.e., unidirectional charge-transport through the column.<sup>130</sup> The formation of these donor-acceptor pairs is favored in apolar solvents. In more polar solvents the triphenylenes alone do not polymerize and consequently donor-acceptor polymers with low DP are formed.

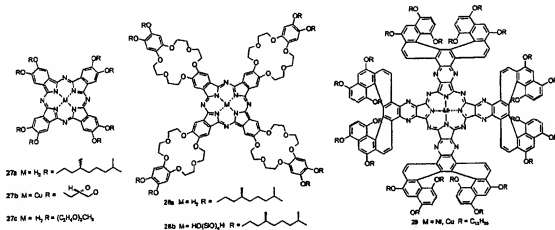
The "loose" way of stacking of the triphenylenes was shown by the absence of a Cotton effect in circular dichroism (CD) experiments for chiral triphenylene 25e in heptane.<sup>131</sup> Even though this chiral molecule does form a supramolecular polymer, the side-chain chirality is not expressed in the column: a phenomenon typical for molecules arranged in an unordered assembly. Mixing of achiral alkoxytriphenylene 25d with a bulky chiral electron acceptor derived from (-)-menthol 3,5-dinitrobenzoate (26) did introduce supramolecular chirality in the columns.<sup>127</sup> The sterically demanding "bulky" menthol group intercalates in the alkyl side-chains of the triphenylene and induces a noncooperative helical twist into the columns (Figure 15), resulting in an induced CD effect in the chromophore of the triphenylene.

Triphenylenes provided with nonionic di(ethylene oxide) side-chains (25f)<sup>132-134</sup> or with ionic alkyl chains (25g)<sup>135</sup> form supramolecular polymers in water.<sup>136</sup> The arene-arene interactions of the aromatic cores allow for the formation of columnar "micelles". At low concentrations the columns are relatively short, and the solutions are isotropic. At higher concentrations the longer columns interact and lyotropic mesophases are formed.<sup>133</sup> Computer simulations showed that in the isotropic solution the polymerization of the discotics is driven by solute-solute attraction and follows the theory of isodesmic linear aggregation; the association constants for dimerization, trimerization, and etc., are equal and the DP of the column thus can easily be tuned by concentration and temperature.<sup>137,138</sup> At higher concentrations the sizes of the columns are influenced by their neighbors, the columns align, and the DP rises rapidly.

Fluorescence studies have shown that the radiative lifetime of 25f increases upon increasing DP, suggesting that the mobile excitons move through the supramolecular polymers and relax at their ends.<sup>139</sup> Insertion of electron acceptors between the triphenylenes accounts for the formation of longer polymers and increases the order within the column. An X-ray diffraction ring with a diffraction spacing of 3.5 Å indicates a short intermolecular distance, a feature not present for undoped samples.<sup>140</sup> A chiral electron acceptor resulted in the formation of a cholesteric mesophase.



**Figure 15.** (a) Apolar (25a-e) and polar (25f-g) triphenylenes and electron acceptor (-)-menthol 3,5-dinitrobenzoate (26). (b) Helical columns based on the donor-acceptor system as studied by Schuster.



**Figure 16.** Extended-core phthalocyanine discotics 27-29.

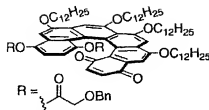
## 2. Phthalocyanines and Porphyrins

With respect to triphenylenes, phthalocyanines have a significantly larger core, in principle generating stronger intermolecular arene-arene interactions.<sup>141</sup> Moreover, their optical and electrical properties can be easily tuned by incorporation of a metal in the core. The aggregation of nonliquid crystalline phthalocyanines in both water<sup>142,143</sup> and in organic solvents<sup>144,145</sup> has been studied intensively in the past; and more recently the formation of Langmuir-Blodgett<sup>146,147</sup> films and the aggregation of liquid crystalline compounds also have been investigated.<sup>148-150</sup> In contrast to the isodesmic aggregation of triphenylenes, phthalocyanines show a nonisodesmic behavior as they preferably dimerize and do not form oligomers until much higher concentrations.<sup>151-156</sup> Experiments on Langmuir-Blodgett films of phthalocyanine 27a have indicated that large columnar aggregates are present (Figure 16), but that they consist of repeating oligomers built up from two to six molecules.<sup>151</sup> Apparently, dimerization significantly lowers the intermolecular affinity of phthalocyanines, and only in phase-separated systems such

as gels, or in the solid, are long supramolecular polymers formed.<sup>157</sup>

Interestingly, it has been possible to obtain helical phthalocyanine polymers. By locking of the position of phthalocyanines, rotation is prevented. Amphiphilic, chiral metallophthalocyanine 27b dissolves molecularly in DMSO, but addition of water results in the formation of a helical dimer.<sup>158</sup> In the twisted helical stacks, rotation is no longer possible because of intermolecular hydrogen bonding. At higher concentrations polymeric fibrous assemblies are formed. For apolar analogues in apolar solvents similar chiral dimers and higher aggregates have been obtained.<sup>159</sup> By providing the phthalocyanine with a periphery of crown ethers<sup>160,161</sup> and chiral alkoxy side-chains (28a), self-assembly in helical aggregates occurs, as was deduced from the emergence of a Cotton effect and large helices observed with electron microscopy at higher concentrations.<sup>162</sup> The side-chains induce a twist in the aggregate because of steric interactions since the aggregates formed by their achiral coun-





30



**Figure 17.** Liquid crystalline disc-shaped helicene **30** and its mode of association into helical columns. (Reprinted with permission from ref 189. Copyright 2000 John Wiley & Sons, Inc.)

terparts are not helical.<sup>163</sup> The helicity of this aggregate could be "turned off" by the addition of potassium salt, overruling the twist imposed by the chiral side-chains, with the ion-dipole coordination of potassium ions to two crown ether rings of two different phthalocyanines. The unwinding of the helical aggregate results in a nonassociating achiral dimer. In contrast, the supramolecular chirality of covalent polymer **28b** remains present upon the addition of potassium ions, illustrating the ease of tuning the properties of supramolecular polymers by external stimuli.<sup>164</sup>

Providing phthalocyanines with chiral bulky helices at the periphery (**29**) also results in helical aggregates.<sup>165</sup> Aggregation in chloroform occurs upon addition of ethanol as was observed with UV-Vis spectroscopy, while CD spectroscopy revealed the helical nature of the columnar aggregates. Calculations have indicated that two phthalocyanines need to be rotated to allow a favorable intermolecular distance of 3.4 Å, because of the bulky helices. As such, phthalocyanines provided with racemic helices cannot stack in such a defined manner, because of the steric hindrance of the racemic side groups. Aggregation of a smaller analogue of **29**, a triphenylene-based porphyrine, has been shown to occur as well.<sup>166</sup>

Polymerization of phthalocyanines in water occurs for derivatives substituted with oligo(ethylene oxide) side-chains (**27c**).<sup>167,168</sup> In the lyotropic mesophases in water supramolecular polymers are present, and a comparative aggregation study between tetraphenylporphyrins and phthalocyanines proved the polymerization of the phthalocyanines to be stronger.<sup>168</sup> The strong arene-arene interactions and the flatness of the aromatic core in the phthalocyanines causes them to aggregate more strongly, also mediated by the additional hydrophobic effect.

Porphyrins are close analogues to the phthalocyanines, and ionic porphyrins can be considered to fall into the class of the chromonics (vide infra), however, nonionic porphyrins also have been shown to aggregate.<sup>168</sup> Also, porphyrins are mainly forming dimers in solution,<sup>169,170</sup> although aggregation into larger aggregates such as fibers has been shown.<sup>171</sup> Within the aggregates the molecules are rotating freely, but use of additional interactions such as intermolecular hydrogen bonding hinders the rotation and generates chiral aggregates.<sup>171</sup>

### 3. Helicenes

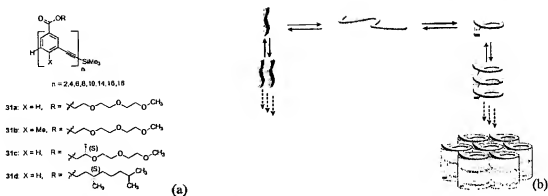
Nonracemic helicene **30** has been shown to form supramolecular polymers, and the helical shape of

their rigid cores renders these columns helical (Figure 17).<sup>172</sup> The high DP at high concentrations in dodecane results in an increase of the viscosity and an increase of the Cotton effect as observed with CD spectroscopy. The helical supramolecular polymer gives rise to a stronger expression of chirality, because the intrinsic shape of the helices generates a tight "intertwined" fit. More detailed measurements have been performed on columns formed by a non-liquid crystalline helicene.<sup>173-175</sup> These supramolecular polymers have been proven to be extremely promising systems for second-order nonlinear optics. They form highly organized Langmuir-Blodgett films in which the chiral polymeric organization makes the second-order NLO susceptibility approximately 30 times larger for the nonracemic material than for the racemic material with the same chemical structure.<sup>176</sup>

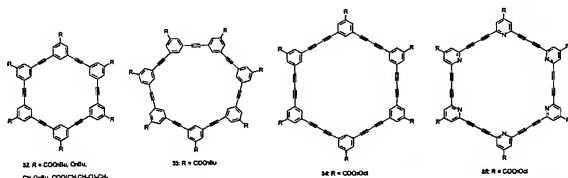
### 4. *m*-Phenylene Ethynylene Oligomers

Whereas helicene **30** studied by Katz<sup>172</sup> is helical under all conditions, the *m*-phenylene ethynylene oligomers studied by Moore are flexible and can reversibly fold into helices. Depending on the substitution pattern, the oligomers fold either into lamellae (**31a**)<sup>177</sup> or into column-forming helices (**31b**)<sup>178</sup> in the liquid crystalline state (Figure 18). In solution the oligomers can be directed to fold from a random coil into a helix.<sup>178,180</sup> Increasing the polarity by addition of water (a nonsolvent for the backbone) results in the polymerization of the helices in helical columns.<sup>181</sup> The polymerization of the oligomers is a cooperative process: a chiral oligomer **31c** creates a homochiral platform for an achiral oligomer **31a** to stack and thus amplifies its chirality to the achiral oligomer. Also, apolar *m*-phenylene ethynylene oligomers **31d** fold into helices.<sup>182</sup> Because of the strongly favored arene-arene interactions in apolar solvents, the helical folding coincides with stabilizing stacking of the oligomers into helical columnar polymers, giving a strong and time-dependent enhancement of the Cotton effect.

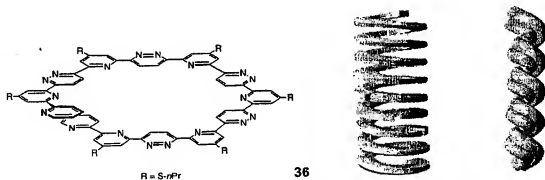
Cyclic *m*-phenylene ethynylene oligomers **32** adopt a completely flat conformation (Figure 19) and form highly stable thermotropic mesophases due to strong  $\pi$ - $\pi$  stacking of the cores.<sup>183</sup> These arene-arene interactions also induce polymerization in solution.<sup>184</sup> The DP depends heavily on the nature of the substituents on the macrocycle.<sup>185</sup> Planarity is a strict requirement for polymerization as the DP is strongly suppressed for nonplanar macrocycle **33**.<sup>186</sup> Butadiene bridged macrocycles with benzenes (**34**) or with pyridines (**35**), the larger analogues of the *m*-phen-



**Figure 18.** *m*-Phenylene ethynylene oligomers as studied by Moore (a), that fold from a random coil in good solvents into helices and columns in poor solvents and into lamellae or hexagonally packed columns in the solid state (b). (Reprinted with permission from ref 178. Copyright 2000 American Chemical Society.)



**Figure 19.** Extended-core *m*-phenylene ethynylene cycles 32–35.



**Figure 20.** Pyridine-pyridazine oligomer 36 studied by Lehn and its proposed mode of aggregation into columns and superstructures. (Reprinted with permission from ref 190. Copyright 2000 John Wiley & Sons, Inc.)

ylene ethynylene macrocycles, have been shown to form columnar polymers as well.<sup>187,188</sup>

### 5. Other Systems

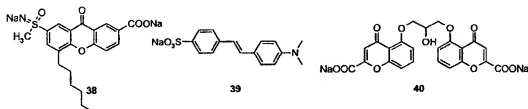
Folding into helices<sup>189</sup> and subsequent polymerization of the helices into columns and larger architectures (Figure 20) is observed for pyridine-pyridazine oligomers (36).<sup>190</sup> Similar to the *m*-phenylene ethynylene oligomers 31, these flexible oligomers adopt a helical conformation because of programmed intramolecular interactions. At higher concentration the polymers self-assemble to give helical fibers, which were visualized with electron microscopy. Upon binding of cyanuric acid, oligoisophthalamides fold to a helical disk, and these disks

also subsequently self-assemble to form fibers at higher concentrations.<sup>191</sup> The controlled use of external stimuli and programmed intermolecular interactions illustrates the power to generate and direct supramolecular polymers.

Ringsdorf showed a nice example of confinement of supramolecular polymers.<sup>192</sup> In cyclohexane, hexacinnamoyl azacrown 37 self-assembles to form supramolecular columnar polymers. The periphery of photopolymerizable groups forms cross-links via photocycloaddition and allows the pre-assembled supramolecular polymer to be transferred into a rodlike covalent polymer (Figure 21). Performing the reaction on molecularly dissolved molecules gives rise to a randomly cross-linked polymer with a lower DP.



**Figure 21.** Hexa-cinnamoyl azacrown with polymerizable side-chains **37** as studied by Ringsdorf, and the photopolymerization into covalent columns in solution.



**Figure 22.** Examples of drug and dye molecules forming chroomic mesophases in water.

As early as 1986, the aggregation in solution of an alkyl modified 2,6,2',6'-tetraphenyl-[4,4']-bipyranilidene was shown, and the self-assembly was related to its thermotropic mesomorphism.<sup>193</sup> The addition of the more polar solvent methanol to methylene chloride induces aggregation into J aggregates. As the nonliquid crystalline compound without the side-chains does not aggregate, it might be concluded that the self-assembly is, in this case, not dominated by the aggregation of the aromatic core. Self-assembly via aggregation of the side-chains occurs, which is fundamentally different from the previously discussed polymers, and generally leads to 3-dimensional growth.

A variety of smaller discotic molecules have been shown to form lyotropic mesophases in either alkane solvents or water. These discotics range from alkyl-oxidybenzopyrenes<sup>194</sup> and hexaesters of hexahydroxybenzene and -cyclohexane<sup>195</sup> to metallo-discogens.<sup>196</sup>

## 6. Chromonics

Discotic molecules provided with oligo(ethylene oxide) side-chains form supramolecular polymers in water. If the discotics are provided with ionic groups the compounds are known as chroomics (for examples see **38–40**, Figure 22).<sup>197,198</sup> Even though chroomics are crystalline and do not form supramolecular polymers in the solid state, we mention them briefly here because of their practical importance and widespread occurrence. A large body of work, dating back to the early part of the 20th century, has been performed on these compounds, and the reader is referred to review articles for detailed information.<sup>197,198</sup> The most common chroomics are drugs and dyes, which explains the early recognition of their aggregation. Their self-assembly in water makes them a highly important type of lyotropic liquid crystal, as it influences their performance. The molecules first self assemble, isodemic, into supramolecular rodlike polymers, followed by the formation of lyotropic mesophases. The rodlike polymers

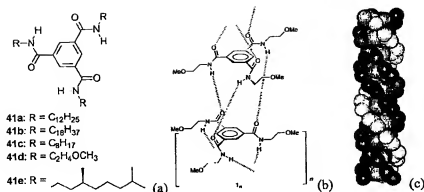
induce a strong increase in the viscosity of the solution, and the dynamic properties of these aggregates leads to rheological behavior typical for entanglement networks.<sup>199</sup> The observations have indicated that chroomics are suited as simple model systems for a broader and deeper insight into the principles of flow.

## B. Hydrogen Bonding

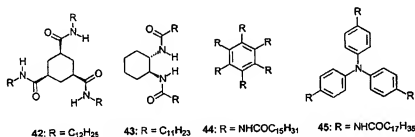
Section V-A has dealt with the formation of supramolecular polymers by nonspecific arene–arene stacking, which generally results in irregular or “loose” stacking. The use of additional steric interactions in these structures allowed for a control over supramolecular order or helicity. In this section we will discuss columnar supramolecular polymers formed by the more specific intermolecular hydrogen bonds.

The main body of work on columnar hydrogen-bonded architectures has been performed on 1,3,5-benzene triamides (**41**), which are C<sub>3</sub>-symmetric molecules consisting of a single benzene ring and 3 side-chains connected via amide bonds.<sup>200,201</sup> The molecules arrange themselves in columns via 3-fold intermolecular hydrogen bonding as proven by X-ray diffraction<sup>202</sup> and infrared spectroscopy. The weak arene–arene interactions of the single central benzene group are subordinate to the strong 3-fold hydrogen bonding. For packing reasons, the intermolecular hydrogen bonds rotate out of the plane, thus inducing helicity in the columns. Achiral compounds **41a–d** form an equimolar mixture of left- and right-handed helical columns, but the homochiral side-chains of chiral discotic compound **41e** introduce an energy difference between left and right-handed columns and bias the helicity.<sup>203</sup> Figure 23 shows the formation of the helical columnar polymers by the polymerization of **41d** in a cartoon-like presentation.<sup>202</sup>

The helical rigid-rod polymers have a high DP even in very dilute solution (10<sup>−6</sup> M in hexane), due to their large association constant (5·10<sup>8</sup> L/mol). When



**Figure 23.** (a) 1,3,5-Benzene trisamides that form columns in apolar solvents via 3-fold intermolecular hydrogen bonding; (b) solid state arrangement of the helical columns; (c) graphical representation of the helical hydrogen-bonded columns. (Reprinted with permission from ref 202. Copyright 1999 Royal Society of Chemistry.)



**Figure 24.** Small discotics that form columnar polymers via intermolecular hydrogen bonding.

chiral (41e) and achiral (41c) molecules are blended mixed columns are formed, and, surprisingly, only one chiral disk (on average) on every 200 achiral disks is enough to bias the helicity of a complete columnar polymer for one helicity. These results are analogous to those obtained in chiral polymers with covalent bonds in the main chain<sup>204</sup> and are explained by a strong intracolumnar cooperative effect via directional hydrogen bonding in polymers with a very high DP. At higher concentrations, the long columns gelate the solvent via lateral intercolumnar interactions,<sup>200,201</sup> reminiscent of the behavior of rigid-rod covalent polymers such as polyaramides and poly( $\gamma$ -benzyl-L-glutamate).<sup>205</sup>

Cis-1,3,5-cyclohexanetricarboxamides (42) are another example of discotic molecules assembling in columns via intermolecular hydrogen bonding (Figure 24).<sup>206</sup> Because of the cis arrangement of the amides, all three can participate in the uni-directional hydrogen bonding. Depending on the type of solvent, the compound either gels the solvent or forms a transparent viscoelastic fluid. No mention is made of the presence of helicity in the columnar aggregates or at a microscopic level, in contrast to the trans-1,2-diaminocyclohexane derived gelators (43), which form chiral supercoiled structures observable with electron microscopy.<sup>207</sup>

Aggregation via hydrogen bonding and formation of columns and lyotropic liquid crystals and gels has also been described for benzenhexamine derivatives 44<sup>208</sup> that assemble via 6-fold intermolecular hydrogen bonding, and for tris(stearylamine)triphenylamine 45<sup>209</sup> that assembles via 3-fold intermolecular hydrogen bonding.

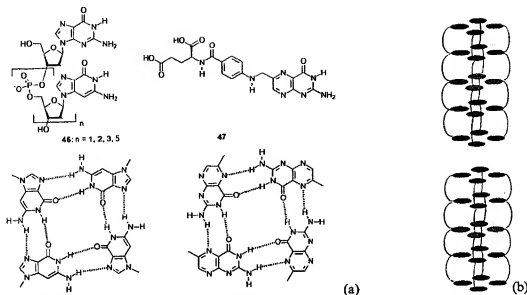
## C. Arene-Arene Interactions and Hydrogen Bonding

Although hydrogen bonds can be employed for the creation of highly ordered columns (section V-B), their use is highly limited to apolar solvents. In contrast, arene-arene interactions allow for supramolecular polymer formation in a large variety of solvents, but without positional control (section V-A). Thus, the combination of arene-arene interactions and hydrogen-bonding should allow for formation of highly ordered supramolecular polymers with high DP in solvents as desired. In this section we discuss such supramolecular polymers. Hydrogen bonding has been utilized both for the formation of the discotic entity itself and as a tool to control the order within the columns. Furthermore, the occurrence of hydrogen bonds allows for a controlled hierarchical growth of the well-defined columns, and subtle tuning of the interactions can be achieved by selection of solvent type.

### 1. Guanine and Pterine Derivatives

The most impressive work on self-assembling chiral discotics has been performed on guanine- and pterine-related molecules by Gottarelli, Spada, and co-workers.<sup>210</sup> These molecules organize in lamellae in the solid state,<sup>211,212</sup> but form disc-shaped tetramers in solution via intermolecular hydrogen bonding. The subsequent stacking of the disks into helical columns has been most elaborately studied. The system is of interest because of its strong similarities to DNA and other biopolymers.<sup>213,214</sup>

Oligomeric deoxyguanosines 46 all assemble into columns in water.<sup>215</sup> Using SANS, the average length



**Figure 25.** (a) Deoxyguanosine oligomers **46** and folic acid **47** and their mode of self-assembly in tetramers; (b) mode of aggregation of eight d(GpGpApGpGpC) molecules. First, self-assembly in "barrels" occurs, followed by stacking of these "barrels" in columns. (Reprinted with permission from ref 222. Copyright 1995 Royal Society of Chemistry.)

of the columns (DP) of freshly prepared samples was determined to be around 6 nm at a concentration of 1% in  $D_2O$ .<sup>210</sup> Increase of the temperature resulted in loss of the cylindrical aggregates. When the sodium salt is used, subsequent cooling does not result in the re-formation of the cylindrical polymers. In contrast, use of the potassium salt does allow for reversible self-assembly. The addition of extra potassium salt even increases the DP; it binds to the inner carbonyls of the G-tetramer and stabilizes the tetramer.<sup>216</sup>

The formation of lyotropic liquid crystalline mesophases by a deoxyguanosine derivative in water was reported in 1988,<sup>217</sup> after which this behavior was found for other monomers and oligomers of deoxyguanosine phosphate.<sup>218</sup> The microscopic textures observed show the presence of cholesteric and hexagonal phases at lower and higher concentrations, respectively. The polymeric columns are formed in a hierarchical manner: first a well-defined "barrel" is formed by the assembly of four oligodeoxyguanosine oligomers, and then these "barrels" stack on top of one another to give the columns (Figure 25 b).<sup>210,215</sup> This stepwise self-assembly process was elucidated using CD experiments, which revealed two melting transitions. Furthermore, it was shown that formation of the liquid crystalline phase depends on the amount of electrostatic repulsive interactions from the phosphate groups and the hydrophilic/hydrophobic balance.

Not only guanosine, but also pterine derivatives, give rise to supramolecular polymers in water.<sup>219</sup> Similar to the guanosines, folic acid **47** assembles in disc-shaped tetramers in water. Addition of sodium or potassium salts aids the tetramerization and induces the aggregation into columns.<sup>220</sup> At the relatively high concentration of 4%, w/w, these columns have an average DP of 9 disks. Melting experiments performed in water and upon the addition of salt showed very interesting results. The

intensity of the Cotton effect was followed as a function of temperature, indicating the amount of chirality present in the columns. In water a single melting transition was detected, whereas in the presence of salt two melting transitions were visible, indicating hierarchical assembly.<sup>221</sup>

Gottarelli, Davis, and co-workers have prepared apolar guanosine derivatives **48a** and **b** for study in organic solvents. In dilute solution in the presence of potassium ions, disc-shaped structures are formed.<sup>222</sup> In chloroform compound **48b** is molecularly dissolved, but upon contact of the organic layer with an aqueous layer containing potassium salts, **48b** extracts the potassium into the organic layer. An octameric potassium complex is formed, consisting of two stacked G-quartets between which a potassium ion is sandwiched via interactions with the carbonyls of the guanosines (Figure 26).<sup>223,224</sup> Upon the addition of more salt the octamers polymerize into a columnar architecture. In this polymer potassium ions and G-quartets alternate in the stacking.<sup>223</sup> The Cotton effect observed for the polymer indicates a helical columnar nature. Apart from the formation of octamers, the formation of decamers has also been observed.<sup>226</sup>

Compound **48b** was shown to display enantioselectivity in the extraction of chiral potassium salts from water into the organic phase.<sup>227</sup> The supramolecular polymer possesses a homochiral helical architecture onto which one of the anionic enantiomers preferentially binds. Intriguingly, for some of the anions the octamer and polymer show opposite selectivity, illustrating the difference in supramolecular chirality of the two. Furthermore, the polymer is capable of inducing a Cotton effect in the achiral potassium *N*-(2,4-dinitrophenyl)glycinate. The use of these polymers as artificial ion channels is currently under investigation, as the apolar side-chains would allow incorporation into a membrane.<sup>224,228</sup> Also,

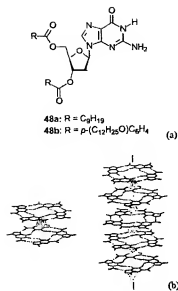


Figure 26. (a) Apolar modified deoxyguanosines, soluble in organic solvents; (b) self-assembly of apolar deoxyguanosines in octamers and polymers upon the addition of potassium ions. (Reprinted with permission from ref 225. Copyright 2001 John Wiley & Sons, Inc.)

these helical columns are ideal supramolecular polymeric architectures for the creation of functional arrays. By providing the guanosines with apolar porphyrins, self-assembly into columns with a periphery of porphyrins was achieved in chloroform by the addition of potassium salt.<sup>229</sup> The formation of such functional polymers using external stimuli offers a unique approach for the creation of bio-inspired self-assembled polymers.

## 2. Hydrogen-Bonded Pairs

Similar to the guanosine and pterine derivatives, intermolecular hydrogen bonding generates discotics based on molecules 49. Two molecules 49 dimerize via quadruple intermolecular hydrogen bonding resulting in an extended-core discotic liquid crystal that stacks in apolar solvents and forms columnar supramolecular polymers.<sup>230</sup> Within these columns the discotics are rotating freely. When two hydrogen-bonding units are connected via a short spacer, a bifunctional molecule is generated (50), capable of forming hydrogen-bonded, supramolecular polymers

in chloroform similar to the bifunctional ureidopyrimidinones 21 discussed in section IV-E.<sup>113</sup> The disks are in an alternating array of disks and spacers, and they stack in apolar solvents forming a columnar polymer. The columns are helical, in contrast to those formed by monofunctional molecules 49 (Figure 27). The presence of a covalent linkage between consecutive layers of the column prevents rotation of the disks. A comparison might be made here to the function of the sugar-phosphate backbone in DNA.

The intrinsic helicity of the columns formed by bifunctional 50 allows chiral side-chains to control for a preferred handedness (50b). The supramolecular polymeric backbone also accounts for a higher DP with respect to monofunctional 49, as could be observed with SANS and an increased thermostability of the lyotropic mesophase in dodecane. The induction of chirality in the helical columns of 50b by the chiral side is a cooperative process via the backbone: the helicity of a racemic mixture of helical columns of achiral 50a is biased when end-capped with monofunctional chiral 49b.

Helical columns of bifunctional ureidotriazines could also be created in water.<sup>230</sup> In water the aromatic cores of compound 52 stack and create a hydrophobic environment that favors the formation of intermolecular hydrogen bonds. The chiral side-chains can express their chirality within the columnar polymer because of the backbone-generated helicity. In contrast, for monofunctional 51 water interferes with the hydrogen bonding and 51 does not dimerize nor polymerize until it reaches highly elevated concentrations. The bifunctional nature of 52 allows for a high local concentration of stacking units. A comparison might be made here to the individual DNA bases that also do not dimerize and stack in water, unless they are connected to a polymer backbone.

## 3. Complexation of Tetrazoles with 1,3,5-Tris (4,5-dihydroimidazol-2-yl)benzene

Another example of supramolecular columnar polymers formed by the combined use of hydrogen bonding and arene-arene interactions are the complexes of tetrazoles and 1,3,5-tris(4,5-dihydroimidazol-2-yl)benzene (53, Figure 28).<sup>231</sup> Four molecules self-assemble to give a supramolecular disc-shaped molecule, which subsequently polymerizes into columns when in nonpolar solvents. Upon formation of a

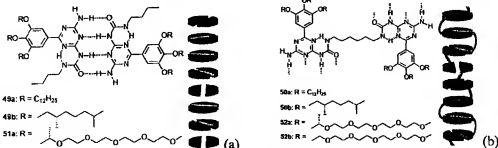
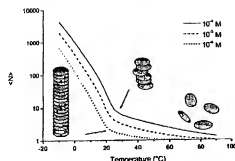


Figure 27. (a) Monofunctional ureidotriazines 49 and 51 and the mode of association of 49 via quadruple hydrogen bonding in a disk and stacking of the disks in columns lacking positional order; (b) bifunctional ureidotriazines 50 and 52 and the helical columns formed by these molecules in which the disks are positionally ordered.





**Figure 30.** Average number of molecules 55, ( $N$ ), participating in one column in *n*-butanol at three different concentrations is given as a function of temperature. Arrows mark the transition from achiral to helical aggregates.

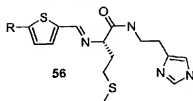
°C as proven by SANS. This stepwise growth of the columns shows great similarity to the self-assembly of the tobacco mosaic virus without the ribonucleic acid strand and will undoubtedly aid in the understanding of biopolymer self-assembly.<sup>238</sup>

In *n*-butanol the average distance between helix reversals in columns containing both 55a and 55b was found to exceed 400 molecules via "sergeant and soldiers"<sup>204</sup> experiments. The high persistence length of the helicity results in strong (400-fold) amplification of chirality. In water, the helix inversions were found to occur after, on the average, every 12 disks, indicating that the helical order within the columns is highly solvent-dependent.<sup>238</sup> In water, the solvent interferes with interactions accounting for helical order at all temperatures, resulting in a lower energy barrier for helix inversions.

## VI. Supramolecular Coordination Polymers and Miscellaneous Systems

Metal coordination has been used to prepare a wide range of supramolecular complexes with geometries varying in complexity from simple cyclic dimers to catenanes, helicates, and cages with intricate geometries.<sup>239</sup> In view of the apparent ease of construction of these well-defined assemblies, the number of 1-dimensional coordination polymers that has been characterized in solution is surprisingly small. There is extensive literature about coordination polymers in the solid state; this is outside the scope of the present review because these polymers do not exist outside the confinement of their crystal lattice. Most soluble coordination polymers, be they linear;<sup>240–248</sup> or hyperbranched;<sup>249,250</sup> are held together by kinetically stable metal–ligand interactions and do not show the dynamic reversibility that is observed in true supramolecular polymers. Kinetically labile coordination complexes of metal ions such as Cu(I) and Ag(I) are required to form such aggregates. The first report of dynamic oligomers using these metals dates from 1992,<sup>251</sup> and it describes stereoregular coordination polymers using peptide-based polydentate ligand **56** containing thienyl, imidazolyl, and thioether donor sites (Figure 31).

The solid-state structure of the complex with silver triflate was determined with X-ray diffraction. On the



**Figure 31.** Peptide-based ligand **56** which forms reversible coordination polymers with Ag(I).

basis of a combination of vapor pressure osmometry and conductivity measurements in methanol, the average DP at 0.14 M concentration was estimated to be approximately 11. The reversibility of association was evident from the concentration dependence of the DP; at low concentrations only a monomeric complex was observed. Coordination complexes of Cu(I) and Ag(I) with phenanthroline ligands **57** have been used to prepare the first constitutionally well-defined coordination polymers from kinetically labile complexes in 1996.<sup>252</sup> It was demonstrated that high-molecular-mass polymers can be obtained from rigid bis(phenanthroline)ligand and Cu(I), if the solvent used cannot act as a competitive ligand for the metal (Figure 32).

The authors showed that ligand exchange takes place instantaneously in a mixture of Cu(I) and Ag(I) model complexes in coordinating solvents such as acetonitrile, whereas in 1,1,2,2-tetrachloroethane no evidence of ligand exchange was observed after several hours. The strategy to obtain the polymer was based on using the latter solvent, in which ligand exchange is slowed as much as possible. Upon titrating a solution of the monomer with  $[Cu(MeCN)_4]PF_6$ , <sup>1</sup>H NMR spectra showed that end groups were present when less than 1 equiv copper salt had been added, and that at a 1:1 stoichiometry, only broad polymer resonances remained.<sup>253</sup> The resulting solutions displayed high viscosities, indicating high molecular masses. Upon further addition of metal salt, the viscosity decreased again. From this experiment, it can be concluded that exchange between free and coordinated Cu(I) ions continues to occur, even in a noncoordinating solvent. When the polymer was precipitated and redissolved, no signs of degradation of the polymer were observed.

A different approach to coordination polymers has been taken by Terech and co-workers, who studied the aggregation of a Cu(II) tetraoctanoate (**58**, Figure 33). Using neutron scattering, it was shown that in apolar solvents the complex molecules assemble in a linear fashion to form threads with a cross section containing approximately 1 binuclear copper complex.<sup>254</sup> Studies in Decalin<sup>255</sup> have shown that under certain conditions, the rheological behavior of this system can be described by the theory of living polymers that has been developed by Cates and co-workers.<sup>256,257</sup> It was suggested that, below a given transition temperature, physical junctions between chains act both as chain extenders and as efficient physical cross-links, resulting in rheological behavior that matches Cates' predictions of reversible polymers in the semidilute (entangled) regime. Above



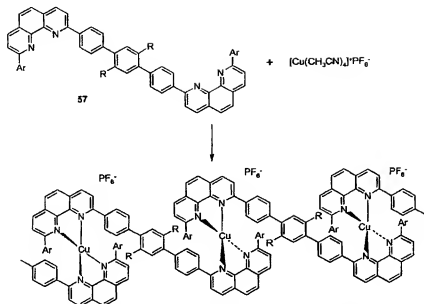


Figure 32. Bifunctional metal complexing **57** and its mode of polymerization upon addition of  $\text{Cu}^+$ .

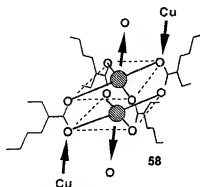


Figure 33. Mode of aggregation of  $\text{Cu(II)}$  tetraoctanoate **58** into linear polymers. (Reprinted with permission from ref 254. Copyright 1992 American Chemical Society.)

$T_{\text{trans}}$ , these physical junctions melt, and the relatively short chains are no longer entangled.

Hunter and co-workers recently reported soluble, high-molecular-weight coordination polymers based on porphyrins.<sup>258</sup> A porphyrin was provided with two pendant pyridine groups and a cobalt atom (which has six coordination sites) in the center. The bifunctional molecule **59** was anticipated to form coordination polymers in the fashion depicted in Figure 34. It was shown by  $^1\text{H}$  NMR diffusion studies that polymeric aggregates were indeed obtained, and aggregation was confirmed by size exclusion chromatography, which showed that **59** forms aggregates which are significantly larger than those of **60**, which cannot associate beyond the dimeric state. Moreover, the size of the aggregate was shown to be dependent on the concentration of the solution. SEC was also used to show that the size of the aggregates could be tuned by addition of increasing amounts of monofunctional compound, incidentally demonstrating the reversibility of the aggregation process. Using the oligomer peaks in SEC that were observed upon

mixing **59** and **60** as calibration, the authors calculated that the aggregates in a 7 mM solution of **59** have an average molecular mass of 136 kDa, corresponding to a DP of about 100. These experiments nicely demonstrate the balance between kinetic stability (required for successful separation by SEC) and the reversibility needed for tuning the DP with monofunctional molecules.

Usually, ion-dipole interactions are insufficiently directional for the formation of linear supramolecular polymers because the functional groups providing the interaction tend to form clusters in such a system. Recently, Gibson and co-workers have shown that the combination of crown ethers and secondary ammonium ions can successfully be employed for this purpose.<sup>259</sup> They designed a system based on Stoddart's finding that 24-dibenzo-crown-8 and dibenzylammonium hexafluorophosphate associate strongly ( $K_a = 2.7 \times 10^4$  in  $\text{CDCl}_3$ ).<sup>260</sup> Association of bifunctional molecules **61** and **62** was investigated by Gibson, and was shown to lead to chain extended aggregates (Figure 35), as was evident from the strong concentration dependence of the viscosity of 1:1 solutions of these compounds in  $\text{CHCl}_3/\text{acetone}$ . On the basis of end group analysis by NMR, the molecular weight of the aggregates was estimated to be 22 kDa for a 2 M solution, whereas at low concentrations the spectrum was dominated by signals of a cyclic dimer. Flexible films and fibers were obtained from concentrated equimolar solutions of **61** and **62**, from which it was inferred that entangled linear aggregates are present in the solid material. The same interaction between secondary ammonium groups and crown ether moieties has been used in dendritic self-assembly.<sup>261</sup>

Li and McGown used the well-studied inclusion behavior of cyclodextrins to obtain nanotube aggregates of cyclodextrins (**63**) and diphenylhexatriene (**64**) (DPH).<sup>262</sup> These reversible, polymer-like aggregates can be formed because two phenyl "head-

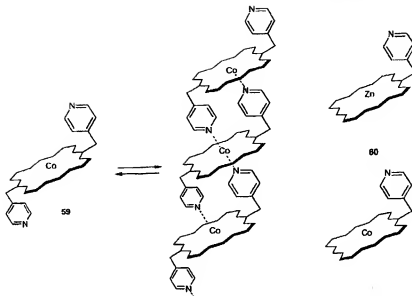


Figure 34. Formation of coordination polymers from porphyrin 59 and two chain stoppers 60.

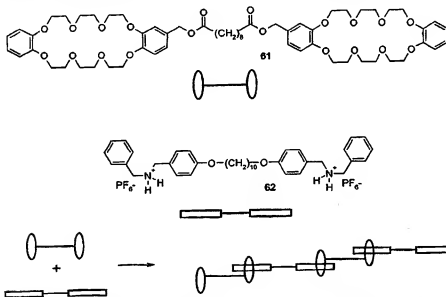


Figure 35. Polymerization via interactions between bifunctional ammonium compounds and bifunctional crown ether derivatives.

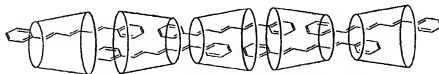
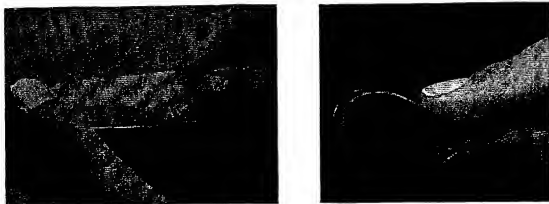


Figure 36. Supramolecular polymer consisting of  $\beta$ -cyclodextrin 63 and DPH 64.

groups" of DPH fit into the cavity of  $\beta$ -cyclodextrin, and the cavity of  $\gamma$ -cyclodextrin can accommodate three phenyl groups. Binding of the phenyl groups of one DPH molecule in two different cyclodextrin cavities (Figure 36), results in polymeric aggregates with an estimated length of 20  $\beta$ -cyclodextrins, or 20–35  $\gamma$ -cyclodextrins, based on light scattering results. Scanning tunneling microscopy of the ag-

gregates on graphite confirmed their nanotube architecture.

The specific inclusion of adamantyl groups in  $\beta$ -cyclodextrin in aqueous environments has been used as binding interaction between adamantyl end-capped poly(ethylene oxide)<sup>263,264</sup> or polyester and a cyclodextrin polymer. Even though the formation of linear chain extended structures was not specifically



**Figure 37.** Supramolecular polymer materials created with the ureidopyrimidone unit. (Reprinted with permission from ref 118. Copyright 2000 John Wiley & Sons, Inc.)

studied – polyfunctionality of the cyclodextrin polymer gives rise to network architectures – the highly defined 1:1 stoichiometry of the interaction and its reversibility make this an interesting system. Interaction between the two polymers has been demonstrated through dynamic light scattering and viscosity measurements. The limiting value of the relaxation time in light scattering measurements (230 ms) was suggested to be related to the lifetime of the inclusion of adamantyl groups in the cyclodextrin cavity.

### VII. Conclusions and Outlook

Roughly fifteen years after the first experiments toward supramolecular polymers (monomeric units held together by specific directional secondary interactions), it can be concluded that a new research area is added to the field of polymer science. The progress in supramolecular chemistry has paved the way to assembling small molecules into polymer arrays: structures that possess many of the well-known properties of “traditional” macromolecules. Because of the reversibility in the bonding, these supramolecular polymers are under thermodynamic equilibrium, and their properties can be adjusted by external stimuli. In this review we have analyzed three different classes of supramolecular polymers, in which hydrogen-bonded systems have been shown to be technologically relevant, having surpassed the state of being merely scientific curiosities. A large variety of applications is foreseen to be feasible, especially as this approach can also be used for the modification of telechelic oligomers or to modify existing polymers. But also, the possibility to tune the properties by simple copolymer formation due to just mixing monomers seems very attractive, whereas hybrids between blocks of macromolecules and supramolecular polymers are easy to prepare. Therefore, novel thermoplastic elastomers, superglues, hotmelts, and tunable polymeric materials are within reach (Figure 37).

Discrete molecules are of interest for their solution properties and their intriguing supramolecular architectures, in which a level of control in two-dimensional structures can be reached, that shows them to be of particular interest as models for natural systems. Their relatively poor mechanical properties,

such as low strength of the supramolecular gels and their phase transitions, gives them a low added-value with respect to covalent polymers as construction materials. However, their strong  $\pi$ - $\pi$  interactions within a column lead to high electronic mobilities, a property that is essential in the development of plastic transistors and photovoltaics.<sup>265,266</sup> Coordination polymers and a number of other approaches show the versatility of the supramolecular polymer approach.

Finally, an important conclusion that arises after discussing the literature on supramolecular polymers relates to the fact that these polymers are also interesting systems to be used by polymer theorists to verify a number of polymer theories. The thermodynamic nature of the supramolecular polymers enables the study of these systems without the kinetic constraints that are normally involved in the study of macromolecules. The future, however, will show the scope and limitations of this new field of supramolecular polymers. We foresee a bright future, and it is now clear that the status of supramolecular polymers has grown from scientific curiosities into systems with technological relevance.

### VIII. Acknowledgments

We acknowledge the many contributions of and discussions with our colleagues Jef Vekemans, Anja Palmans, Felix Beljer, Ronald Lange, and Ky Hirschberg. The research presented has been supported by the Eindhoven University of Technology, DSM Research, and The Netherlands Organization for Chemical Research (CW), with financial aid from The Netherlands Organization for Scientific Research (NWO), the National Research School Combination Catalysis (NSRC-C), and the Dutch Polymer Institute.

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## [総合論文]

## 超構造高分子液晶—自己組織化による分子配向構造の形成と機能化

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(受付 1997 年 6 月 3 日・審査終了 1997 年 6 月 24 日)

P.D. 1997  
p. 855-862 = 8

**要 旨** 「明確な構造を有する液晶が水素結合による分子認識プロセスで形成可能」という新しい概念・手法により構築されたさまざまなタイプの超構造高分子液晶について、それらの構造と性質、その特徴について述べる。水素結合の形成プロセスにより、複数のシンプルな構造の分子コンポーネントから側鎖型・主鎖型・ネットワーク型などの、さまざまな高分子液晶が得られ、安定した液晶挙動を示した。さらに、複合型・ホスト・ゲスト型などの新しい超構造高分子も作製された。複合型構造の高分子は、ビリシン環を導入することにより骨格上での分子認識能を付与したポリアミドと安息香酸誘導体から得ることができた。これらは非共有結合で構築するため、構造形成は自発的な分子自己組織化プロセスにより行うことができる。また構造も動的であり、三次元ネットワーク構造でも液晶相を発現し、可逆的な回転移動が観察された。さらに、配位結合の形成を利用した自己組織性主鎖型液晶高分子も得られた。

## 1 はじめに

生体高分子は、核酸・タンパク質・多糖類、どれも水素結合部位を有し、これらの関与する相互作用により、精密な高次構造形成・動的な機能発現が可能となっている。これに対し、合成高分子は、ポリエチレンに代表されるように、水素結合部位をもたないものが多い。このため、機械的特性や安定性に優れているが、精密な機能発現という点では生体高分子に遠く及ばない。一方、液晶は動的な分子配向体であり、分子が集合して動的な分子組織体形成する生体系と、ある意味で同じ特徴を有しているといえる。これまで多くの研究がなされてきたのは、主として合成分子を用いた液晶についてである<sup>1-11)</sup>。この合成系の液晶においても、分子組織性とその動的な特徴を活用することができれば、機能性分子システムとして、表示デバイスや高強度・高弾性率材料のみならず、さまざまな分野においての発展が期待できる。しかしながら、合成系の液晶材料においては、さまざまな共存する分子間に相互作用が協調的に働いている生体系のようなシステムを目指す分子設計は、行われてこなかった。このような設計においては異種分子間に働く相互作用の制御が鍵となると考えられる。しかし、液晶性低分子あるいは高分子の分子構造構築にこれまで用いられてきたのは共有結合であった。1989 年、「明確

な構造を有する液晶が、非共有結合である水素結合による分子認識プロセスで形成可能」という液晶分子の設計に関する新しい概念・手法が示されて以来<sup>12)</sup>、異種分子間の選択的相互作用により超構造を形成する側鎖型・主鎖型・ネットワーク型などの、さまざまなタイプの高分子液晶が開発されてきた（ここでは異種分子間空間に働く水素結合などの比較的強い相互作用により得られる明確な構造を有する液晶性分子複合体を超分子液晶あるいは超構造液晶とする）<sup>13-20)</sup>。さらに主鎖型・側鎖型の両方の特徴を有するタイプ<sup>21)</sup>、水素結合の活用と発展系としてのホスト・ゲスト系<sup>22)</sup>、両親媒性メッセン分子の自己組織化<sup>23)</sup>、ポリマーブレンド<sup>24)</sup>も最近報告されている。ここで用いられる水素結合は、安定性・方向性にも優れており、分子の自己集合・自己組織化プロセスを用いて形成させることが可能である。また、結合の形成・解離を可逆的に行わせることができる。さらに、イオン相互作用・電荷移動相互作用、さらに配位結合形成による自己組織化などを用いて、新しい高分子液晶も構築されている<sup>25-31)</sup>。低分子構造を有する超分子液晶<sup>32,33)</sup>、また 1994 年以前の超構造高分子液晶の進展については、いくつかの総説・解説に詳しい<sup>34-36)</sup>。本稿では特に 1995 年以降に報告された高分子タイプの超構造液晶の展開について筆者の研究を中心に述べる。

## 2 超構造を有する高分子液晶

まず、分子の集合により得られる超構造高分子液晶の概念図を Fig. 1 に示す。高分子側鎖に水素結合により

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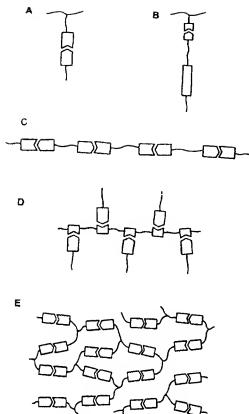


Fig. 1. Schematic illustration of the structures of supramolecular liquid-crystalline polymers obtained by hydrogen bonds: (A) and (B) side-chain types; (C) main-chain type; (D) combined type; (E) network.

剛直なコア構造を形成するもの (Fig. 1A)<sup>33, 11)~16)</sup>, 側鎖構造を水素結合により, “グラフト”させて側鎖型高分子液晶構造とするもの (Fig. 1B)<sup>17)~21)</sup>, 二官能水素結合性分子から主鎖型の液晶高分子構造を形成させるもの (Fig. 1C)<sup>22), 23)</sup> などが報告されている。Fig. 1D は単純に側鎖型・主鎖型に分類できない新しいタイプの超構造液晶高分子である<sup>24)</sup>。Fig. 1E は, 水素結合のダイナミクス (動的性質) を利用した液晶性分子ネットワークである<sup>25)~29)</sup>。これらの構造構築に用いることのできる水素結合の種類を Fig. 2 に示す。これらは, 比較強い (40~50 kJ/mol 程度) 結合エネルギーを有しており, 安定な分子複合構造を形成することができる。これまで主としてカルボキシル基/ピリジル基間の一重の水素結合により種々の液晶性超分子コンプレックスが構築されてきた。また, Fig. 2D に示すカルボキシル基/イミダゾール基の組み合わせは, 最近その有効性が示されている<sup>35)</sup>。今後, 液晶の多様な機能を開発していくには, ささまざまな化学プロセスを可能とする官能基を有する分子の組織化・機能化が重要なポイントと考えられる。そこで, 多点で水素結合できるように官能基を導入した複

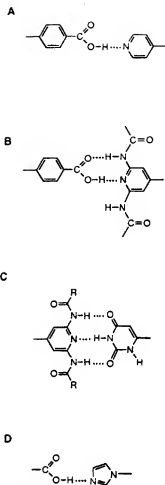
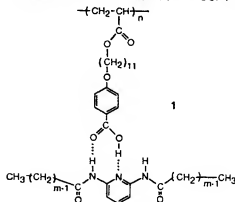
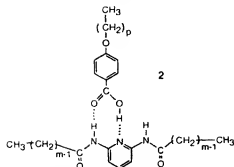


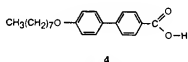
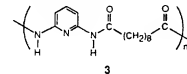
Fig. 2. Hydrogen bonds used for the preparation of supramolecular liquid crystals.

素環に番目し, カルボキシル基/アミノピリジル基間に形成する二重の水素結合による超分子液晶を開発した<sup>10), 30), 31)</sup>。1 の側鎖に形成している水素結合メソゲンとは, 単純な棒状・円盤状の構造をとっていない。これと類似の構造を有する低分子 2 の液晶コンプレックスは, 微妙な化学構造の違いで, ディスコチックあるいはカラミチックな液晶相を発現する<sup>30), 31)</sup>。このことに加え, 1 のメソゲン基はさらに, 手が横に広がったような構造を





もっているためメソゲンの前の向きが主鎖骨格に対し、一定の方向性を有するとも考えられ、ユニークな自己組織体になることが期待される。



2,6-ジアミノピリジンと脂肪酸ジカルボン酸からポリアミド3を合成した<sup>10)</sup>。このポリアミドは、ナイロンのジアミン部分の脂肪酸を複素環に変えた“Heterocyclic Nylon”構造といえる。これにより、主鎖骨格上での水素結合による分子認識が可能となった。このポリアミド3は単独では全く液晶性を示さず、融点が222℃に見られる。ビフェニルカルボン酸4は単独では二重化して260℃まで液晶性を示すが、3と複合体を形成することにより、212℃で融解し、350℃以上まで液晶性を示す超構造高分子複合体5となった。X線解析によると、Fig. 3に示すようなスメクチックA液晶構造をとっていることがわかった。ここで興味深いのは、液晶高分子としては主鎖型・側鎖型に単純に分類できないユニークな構造であること、また、かなりの高温まで液晶相が安定化したことである。5においては、繰返し単位当たり

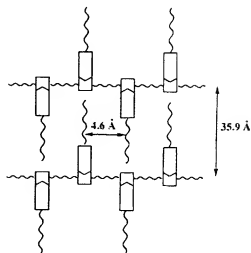
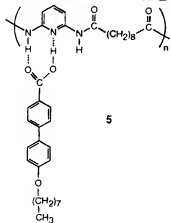
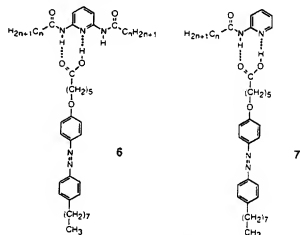


Fig. 3. Molecular arrangement of supramolecular mesogenic polyamide 5.



一つのアミド基が超分子形成には使われず余っている。アミド基は連鎖的な水素結合を形成することが、芳香族ポリアミドなどで知られている。これが液晶相の安定化に役立っていると考えられる。アミド基による水素結合の液晶性に対する効果を検討するために、超分子複合体6および7を作製した<sup>11)</sup>。6と7は各々アゾベンゼンメソゲン基を有しているが、6は超分子形成に使われないアミド基を一つ有している。これらの液晶性を比べたところ、液晶性発現と無関係と思われるアシルアミノ基を余分に有している6の方がより高温で安定な液晶性を示した。具体的には6は昇温時111～123℃まで、また7は昇温時67～107℃の範囲でそれぞれスメクチック液晶性を示した。赤外吸収測定により6の超分子形成に関与していないアミド基は連鎖的な水素結合を形成していることがわかった。すなわち、Fig. 4に示すように、超分子形成の水素結合とアミド基による連鎖的な水素結合という2種の異なるタイプの水素結合が協調して、より安定な分子組織体を形成していることがわかった。5においても同様な効果が発揮されているものと思われる。

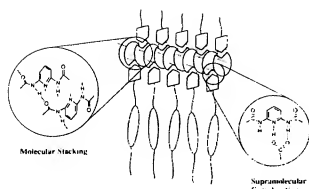
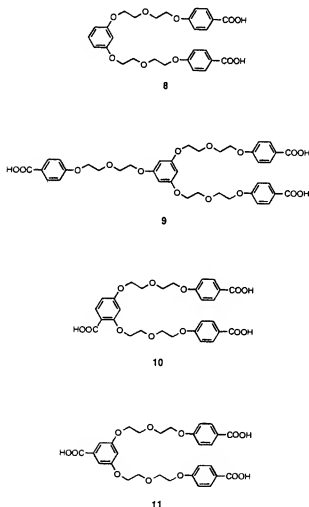
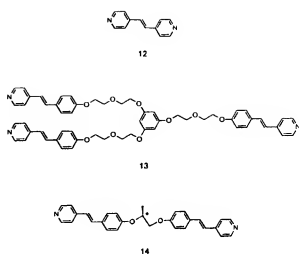


Fig. 4. Molecular association and stabilization for supramolecular mesogenic complex 6 through synergistic cooperation of two types of hydrogen bonds.



### 3 液晶性分子ネットワーク

水素結合を用いると、自己組織化プロセスにより、小さな分子パーツから巨大な三次元構造を比較的簡単に構築することができる<sup>39)</sup>。さらに、水素結合の特徴はそのダ



イナミクスにある、すなわち共有結合と異なり、相互作用ユニット間の組み替え・交換が可能となっている。このような特性を活用して、まず、側鎖に安息香酸部位を有するポリアクリレートと二官能のビビリジンから、液晶性を示す三次元分子ネットワークを構築した<sup>24)</sup>。このような三次元液晶構造は、液晶性を単独では全く示さない低分子同士の集合によっても形成させることができた<sup>25)~29)</sup>。分子8~11は二官能あるいは三官能水素結合ドナーである。これらと、二官能あるいは三官能水素結合アクセプター12~14を組み合わせて、分子自己集合させることにより、ネットワーク構造を有する水素結合性分子複合体が得られた。三官能性分子9~11は、二官能性分子8をもとに、スペーサーを有する安息香酸あるいはカルボキシル基で修飾したものと考えられる。まず、8と12すなわち二官能性分子同士の場合、8の折れ曲がった形から、高分子構造とループ構造が共存する分子集合体になることが予想される。このコンプレックスは、結晶化せず、比較的広い温度範囲で、ネマチック相とスメクチックA相を示した。分子構造が対称性の良い9と12のコンプレックスはスメクチックA相のみを、冷却時、176から156℃で示すが、非対称性の10と12からなるコンプレックスはネマチック相のみを示す。これらは、安定なコンホメーションをとる各分子コンポーネントが水素結合により接続するモデルを組むことにより説明できた<sup>23), 26)</sup>。例えば、三官能性分子同士の、9と13の組み合わせでは、各々の分子はフォーク型のコンホメーションが安定であるためスメクチック相が発現する (Fig. 5)。また、キラルな分子14と非対称性分子10を組み合わせた場合は、コレステリリック液晶構造を有するネットワークとなった。さらに、この構造は冷却時ガラス化してコレステリリック構造を保持したフィルムとなった<sup>27)</sup>。これらの水素結合性ネットワークは、昇温・降温を繰り返した場合、液晶状態と等方性液体状態を可逆的に示した。これは、Fig. 6

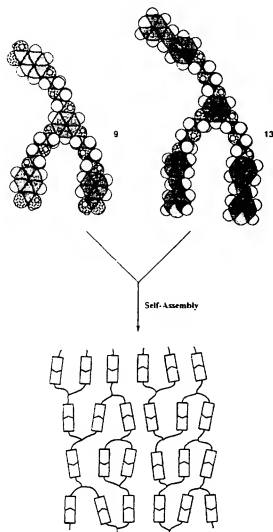


Fig. 5. Induction of a smectic A phase by self-assembly of tri-functional hydrogen bonding molecules of 9 and 13.

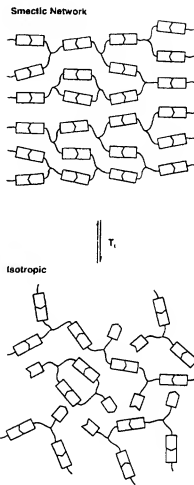
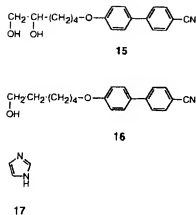


Fig. 6. Reversible phase transition of a supramolecular liquid-crystalline network between nematic and isotropic states.

Table 1. Liquid crystalline properties of supramolecular polymeric networks

Complexes	Phase transition behavior <sup>a)</sup>															
	Heating						Cooling									
8/12	G	100 <sup>b)</sup>	G	104 <sup>b)</sup>	K	156	I	I	151	N	148	S <sub>A</sub>	81	G		
9/12					K	194	I	I	176	S <sub>A</sub>	156	K				
10/12			G	153 <sup>b)</sup>	K	182	I	I	175	N	138	G				
11/12					K	207	I	I	188	K						
9/13					K	144	S <sub>A</sub>	162	I	I	157	S <sub>A</sub>			129	K
9/14					K	150	Ch	177	I	I	171	Ch			75	G
10/14					G	142	Ch	180	I	I	174	Ch			62	G

<sup>a)</sup> Transition temperatures (°C). G, glassy; K, crystalline, S<sub>A</sub>, smectic A; nematic; Ch, cholesteric. <sup>b)</sup> Cold crystallization occurs at these temperatures.



に示すように、相転移時に水素結合が可逆的に形成・切断しているためと考えられる。共有結合のみからなるネットワークと根本的に異なる特徴である。分子全体が三次元構造に組み込まれているわけではないが、分子15とイミダゾール17から、水素結合がネットワーク化した分子組織体が得られた<sup>31)</sup>。15は、アルコキシシアノフェニルの末端にジオール基を導入したもので、単独ではネマチック液晶性のみを示す。しかし、水素結合性分子であるイミダゾールと複合化して、スメクチックA液晶相を広い温度範囲で示す。これに対し、ヒドロキシル基をつだけ有する分子16とイミダゾールでは、スメクチック相は示さなかった。このことは、ジオール基とイミダゾール分子により水素結合ネットワークが形成され、層状の分子組織構造となっているためと考えられる。

#### 4 液晶性ポリマーブレンド

水素結合をポリマーブレンド系に導入すると、高分子間の相溶性を高めたり、分子配向の誘起などによる性能の向上が期待できる。従来の液晶性ポリエステルは、非液晶性高分子との相溶性に問題があり、これらのポリマーアロイは分子コンジョイントとして、非相溶の状態では使われていた<sup>32)</sup>。我々は、水素結合により相溶性を改善した液晶性ポリマーブレンドとして、水素結合アクセプターとしてビリジル基を側置換基として導入したポリエステル18と水素結合性高分子であるポリビニルフェノール19からなるブレンドを作製した<sup>33)</sup>(Fig. 7)。このブレンドは分子間水素結合の部分的な形成により相分離は観察されなかった。例えば、ビリジル基とフェノール基のモル比が38:62のブレンドの場合、100℃から149℃まで均一で安定なネマチック液晶相を示した。また、他の興味深い例として、超分子的な考え方で設計された非液晶性のポリマーブレンドが報告されている<sup>34)</sup>。分子設計をより進めれば、三次元網目構造を有する加工可能な機械的性質あるいは環境応答性に優れた材料となることが期待できる。

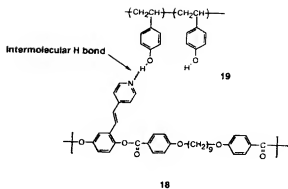


Fig. 7. Liquid-crystalline hydrogen-bonded polymer blends derived from thermotropic polyester 18 and poly(4-vinylphenol) 19.

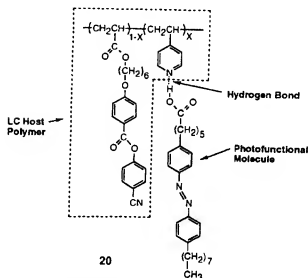


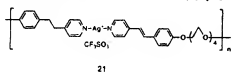
Fig. 8. Structure of hydrogen-bonded host-guest liquid-crystalline system 20.

#### 5 ホスト-ゲスト型高分子液晶

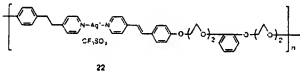
機能性ゲスト分子を高分子液晶ホストの異方場の中に導入して配向させ、機能性材料とするシステムがホスト-ゲスト高分子液晶系であるが、これによりフォトクロミック材料<sup>35)</sup>や非線形光学材料<sup>36)</sup>がつくられている。水素結合システムは、分子間に強い相互作用が働くため、前項でも述べたように、様々な分子を相溶させることができる。したがって、機能性ゲスト分子とホストの間に水素結合を導入することは興味深い。高分子コンプレックス20(Fig. 8)は、光異性化するアゾベンゼン分子を水素結合により高分子液晶中に導入して光応答性材料としたものである<sup>37)</sup>。この場合、単純な混合系よりも相溶性良く、また共重合系よりも容易にゲスト分子を導入することができる新しいタイプのホスト-ゲスト系となった<sup>38)</sup>。また、単純な混合系よりも優れた光応答性が観察された<sup>39)</sup>。

## 6 配位結合形成プロセスによる自己組織性高分子液晶

金属錯体液晶(メタロメソゲン)の開発が盛んに行われている<sup>44)~47)</sup>。配位結合形成を水素結合形成のように自発的に起こすことができれば、高分子構造のメタロメソゲンを自己組織化プロセスで容易につくることができる。スチルバゾリル基をスペーサーでつないだ二官能の非液晶性分子はトリフルオロ酢酸銀と混合すると、高分子構造を形成し、液晶性を発現した<sup>31)</sup>。得られた高分子コンプレックス 21 は、昇温時 185~210°C でスメックチック A 相を示した。また、直線性に欠ける二官能分子から得られたコンプレックス 22 は、210~78°C でモノトロピックなスメックチック A 相を示した。



21



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## 7 おわりに

水素結合のような比較的強い相互作用を駆動力として分子自己組織化プロセスにより、異種分子を複合化させると、単独の分子コンポーネントとは異なる新しい分子(超分子)として配列し、液晶性などの性質を発揮する高分子が得られる。このような手法は、高分子材料の設計に広く適用できる。これを用いて、省エネルギープロセスにより、さまざまな精密構造・高度な機能を有するマテリアルをつくり出していくことが可能であると考えている<sup>48), 50)</sup>。

謝辞 本論文で述べた研究の一部は、文部省科学研究費補助金重点領域研究「新高分子ナノ組織体」(No. 277/08246101)の補助により行われた。

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#### [Comprehensive Papers]

#### Supramolecular Liquid Crystal Polymers. Formation of Molecular Self-Organized Structures and Their Functionalization

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Structures and properties of a variety of supramolecular liquid-crystalline polymers are described. Self-organization processes of several hydrogen-bonding molecular components result in the formation of mesogenic structures of side-chain and main-chain polymers, networks, and a host-guest system. Furthermore, a novel structure of supramolecular polymers that are not simply classified as side-chain or main-chain polymers has been obtained from a *heterocyclic nylon* capable of molecular recognition and benzoic acid derivatives. Such supramolecular materials show dynamic properties. For example, three-dimensional networks show liquid crystallinity and reversible phase transitions. The formation of coordination bonding has also been used for the preparation of self-organized liquid-crystalline polymers.

**KEY WORDS** Liquid Crystal / Liquid Crystal Polymer / Hydrogen Bonds / Self-Assembly / Self-Organization / Supramolecular Chemistry /

(Received June 3, 1997; Accepted June 24, 1997)

[*Kobunshi Ronbunshu*, **54**(12), 855—862 (1997)]





from the fact that, not employing carbohydrate building blocks at all, minimal use of protecting groups is needed.

Received: June 18, 2001 [Z17306]

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## Supramolecular Hydrogen-Bonded Oligo(*p*-phenylene vinylene) Polymers\*\*

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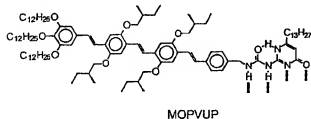
In plastic electronics,  $\pi$ -conjugated oligomers and polymers are applied as advanced materials in a manifold of electro-optical devices such as light-emitting diodes (LEDs),<sup>[1]</sup> field-effect transistors (FETs),<sup>[2]</sup> and important for the present study, solar cells.<sup>[3]</sup> Oligomers possess, due to their well-defined chemical structure, specific electronic and optical properties.<sup>[4]</sup> However, the material properties of oligomers are generally secondary to those of their polymeric analogues, since entanglements of macromolecular chains, which are responsible for the typical polymer properties, are lacking. An attractive approach would be to combine the well-defined character of  $\pi$ -conjugated oligomers with the processability of polymers.

Recently, we reported on supramolecular polymers based on the dimerization of strong quadruple hydrogen-bonding self-complementary 2-ureido-4[1H]pyrimidinone units ( $K_{\text{ass}} = 6 \times 10^7 \text{ M}^{-1}$  in chloroform),<sup>[5]</sup> which exhibit real macroscopic polymeric properties such as an increase of viscosity.<sup>[6]</sup> Improvement of material properties of low molecular weight telechelic polymers was therefore realized.<sup>[7]</sup> These recent developments pave the way to combine the finest properties of conjugated oligomers and polymers by incorporating well-defined  $\pi$ -conjugated moieties in these hydrogen-bonded polymeric assemblies. Furthermore, it provides easy access to multifunctional copolymers by simply mixing the different components containing the quadruple hydrogen-bonded units. A few examples of the combination of  $\pi$ -conjugated oligomers with hydrogen-bonding motifs have been reported. Self-assembled fibers of mono- and bithiophene urea compounds have been described which show efficient charge transport.<sup>[8]</sup> More recently, mono- and bifunctional oligo(*p*-vinylene phenylene)s, (OPV)s, functionalized with ureido-s-triazine have been reported that form stacks in dodecane.<sup>[9]</sup> In a previous paper we disclosed monofunctionalized ureido-pyrimidinone with OPVs (MOPVUP) and hydrogen-bonded  $\pi$ -conjugated dimers were obtained.<sup>[10]</sup>

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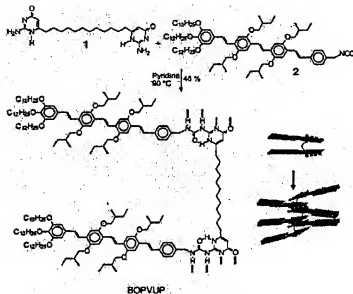
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\*\* This work was supported by Netherlands Organization for Scientific Research (NWO) and the Royal Netherlands Academy of Arts and Sciences. The authors thank Michel Fransen for the synthesis of the starting materials, Joost van Dongen and Xianwen Lou for matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS measurements, Pascal Jonkhoeij for atomic force microscopy (AFM) measurements, and Dr. Rint Sijbesma for fruitful and helpful discussions. Prof. Dr. Jun C. Hummelin is acknowledged for a generous gift of phenyl-[6,6]-C<sub>61</sub>-butyric acid methyl ester (PCBM).



Here we report on the synthesis and electronic properties of bifunctional ureido-pyrimidinone BOPVUP, which contains well-defined  $\pi$ -conjugated oligomers (see Scheme 1). The applicability of these processable  $\pi$ -conjugated supramolecular polymers in a photovoltaic device shows for the first time that supramolecular concepts can be used in electronic devices.

Target supramolecular polymer BOPVUP was obtained in 45 % yield by reaction of isocyanate **1**<sup>[10]</sup> with diisocytosine derivative **2**<sup>[11]</sup> in dry pyridine at 90 °C (Scheme 1) and has



Scheme 1. Schematic representation of the synthetic protocol used to prepare the supramolecular polymer BOPVUP.

unequivocally been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, FT-IR, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS, and elemental analysis. In this compound, two OPV-ureido-pyrimidinone units are linked through a dodecyl spacer at the 6-position of the isocytosine rings. BOPVUP forms supramolecular polymers in solution by strong association of the hydrogen bonding units. MALDI-TOF MS analysis indicates no contamination with a mono-adduct ( $M_r = 3062.62$ )  $m/z$  3063.29 (Figure 1 b). The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  shows a strong downfield chemical shift of the N-H protons to  $\delta = 13.1$ , 12.1 and 10.9 (Figure 1 a), in agreement with the keto-tautomer. A dilution experiment shows no change in chemical shift, while no cyclic structures are observed. The association constant, is similar to that of other ureido-pyrimidinones, namely  $10^4 \text{ M}^{-1}$ . This value deter-

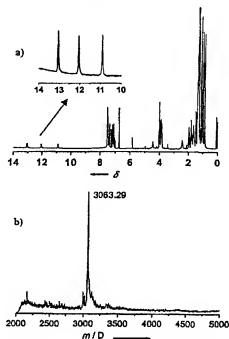


Figure 1. a)  $^1\text{H}$  NMR spectra of BOPVUP recorded in  $\text{CDCl}_3$ ; b) MALDI-TOF MS spectra of BOPVUP.

mines the virtual degree of polymerization, which is calculated to be about 10000 at a concentration of  $1 \text{ M}$ .<sup>[1]</sup>

UV/Vis and fluorescence spectra were recorded in chloroform and dodecane solutions ( $\sim 10^{-4} \text{ M}$ ) at room temperature (Figure 2). For both solutions, the electronic absorption

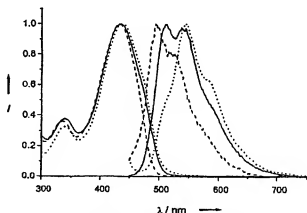


Figure 2. Electronic absorption and emission spectra of BOPVUP; in dodecane (solid line); in chloroform (dashed line) and in a film (dotted line).

maximum is located at  $\lambda_{\text{max}} = 432 \text{ nm}$  corresponding to the  $\pi-\pi^*$  transition of the OPV units. Fluorescence spectra show an emission maximum at  $\lambda_{\text{em,max}} = 494 \text{ nm}$  in chloroform and two emission maxima at 510 and 536 nm in dodecane. Presumably, in chloroform no electronic communication between the two OPV units exists, because the absorption

and emission maxima are similar to that of the monofunctional species MOPVUP in the same solvent.<sup>[10]</sup> The red shift in the emission maxima found in dodecane indicates that the OPV units are then aggregated. The Cotton effect (anisotropy factor:  $g = 1.86 \times 10^{-4}$ ) found for BOPVUP in dodecane by using circular dichroism (CD) spectroscopy is relatively weak compared to that for MOPVUP ( $g = 6.74 \times 10^{-4}$ ), indicating that the aggregates for BOPVUP are not highly organized.

Cyclic voltammetry studies of BOPVUP performed in dichloromethane show reversible electrochemical oxidation processes at  $E_{1/2} = 0.71$  V versus SCE, which are comparable to those of structurally related tetra(*p*-phenylene vinylene)s.<sup>[12]</sup> It is noteworthy that the hydrogen bonds do not participate and are not detrimental for the redox processes.

Photovoltaic devices can be constructed of OPV moieties in combination with  $C_{60}$  derivatives in which the  $\pi$ -conjugated oligomers act as electron donors and the fullerenes as acceptors.<sup>[14, 15]</sup> To illustrate that this hydrogen-bonded supramolecular  $\pi$ -conjugated polymer can be used in electrooptical devices, the photovoltaic properties were investigated. When BOPVUP was dissolved in toluene, highly viscous solutions were obtained, typical for polymers. These solutions could be spin-coated on glass substrates giving good quality films. Atomic force microscopy (AFM) images show that these supramolecular polymeric films are smooth with height variations in the order of 10 nm, which is similar to those reported for poly(*p*-phenylene vinylene)s (PPVs).<sup>[14]</sup> The electronic absorption spectra of these films display a maximum at  $\lambda_{max} = 438$  nm. No CD effect was obtained, which indicated that the films are amorphous resulting in a relative high fluorescence.

Photoinduced absorption (PIA) measurements on spin-coated thin films of BOPVUP ( $\lambda_{ex} = 438$  nm) reveal a band at 1.8 eV that resembles that in the OPV triplet-triplet spectrum. Moreover the photoluminescence of BOPVUP was clearly visible at 2.35 eV. Upon mixing methanofullerene phenyl-[6,6]-C<sub>61</sub>-butyric acid methyl ester (PCBM, inset Figure 3) as electron acceptor in the spin-coated films of

and high energy (HE) absorption bands of the OPV<sup>++</sup> radical cation at 0.78 and 1.52 eV<sup>[13]</sup> and the absorption of the methanofullerene radical anion at 1.24 eV. No photoluminescence for the fullerene moiety was discernable under these conditions, which indicated efficient electron transfer. Varying the modulation frequency from 30 to 3800 Hz revealed that the average lifetime of the charge-separated state is in the order of milliseconds.

Photovoltaic cells were prepared by spin coating a mixture of BOPVUP and PCBM in a ratio of 1:2.8 (by wt) from chlorobenzene onto a transparent ITO front electrode (140 nm) covered with a conducting layer of polythiophenediethiophene polystyrenesulfonate (PEDOT:PSS, 90 nm) and depositing an aluminium back electrode (100 nm) in vacuum. The dark current and photocurrent of the device under white-light illumination ( $88 \text{ mW cm}^{-2}$ , 400–800 nm) reveal promising characteristics (Figure 4). The *I*/*V* curves of

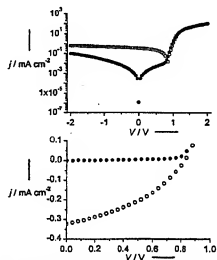


Figure 4. *I*/*V* curves of an ITO/PEDOT:PSS/BOPVUP:PCBM/Al device in the dark (●) and under white-light illumination (○).

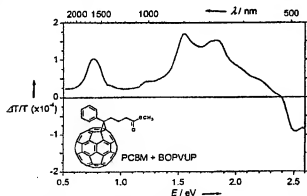


Figure 3. Photoinduced absorption spectra of a mixed BOPVUP:PCBM film (structure of PCBM is shown in the inset).

BOPVUP (BOPVUP:PCBM = 1:2.8 by wt) complete quenching of the OPV fluorescence was observed. PIA measurements revealed the characteristic low energy (LE)

the ITO/PEDOT:PSS/BOPVUP:PCBM/Al device show an excellent diode behavior with a rectification ratio (RR) of  $1 \times 10^3$  at  $\pm 2$  V. The high RR shows that the device has no shunts. A short circuit current of  $I_{SC} = 0.32 \text{ mA cm}^{-2}$  and an open circuit voltage of  $V_{OC} = 0.82$  V were measured. The fill factor, defined as  $(I_{max} V_{max}) / (I_{SC} V_{OC})$ , where  $V_{max}$  and  $I_{max}$  are the voltage and current at maximum power, is 0.39. The values of  $I_{SC}$  and  $V_{OC}$  are favorable compared to those previously reported for solar cells based on  $\pi$ -conjugated oligomers or polymer and fullerene,<sup>[12, 13, 15]</sup> although there has been substantial progress recently by introducing an interfacial layer at the Al electrode.

In conclusion, we have achieved the synthesis of a functional supramolecular hydrogen-bonded  $\pi$ -conjugated polymer that exhibits real macroscopic polymeric properties. A photoinduced charge-separated state was generated within spin-coated blends of the supramolecular polymer with PCBM, and promising photovoltaic devices were obtained. These results create multiple possibilities for using supra-

molecular architectures in electronic devices in which the well-defined character of  $\pi$ -conjugated oligomers is combined with the material properties of polymers

### Experimental Section

**BOPVUP:** Under an argon atmosphere, diisocytosine compound 2 (0.03 g, 0.07 mmol) was dissolved in anhydrous pyridine (5 mL) and heated to 90°C. A solution of OPV-isocyanate 1 (0.20 g, 0.15 mmol) in anhydrous pyridine (10 mL) was added and the reaction mixture was stirred overnight at 90°C. The solution was subsequently cooled to room temperature and the pyridine was removed by evaporation under vacuum. The residue was purified by column chromatography (silica gel, ethyl acetate then  $\text{CH}_2\text{Cl}_2$  to remove impurities and finally  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (97/3, v/v) to collect the desired product) to afford BOPVUP as an orange solid (95 mg; 45% yield). UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 432 nm (258 000  $\text{m}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR (400 MHz,  $[\text{D}]\text{CHCl}_3$ , 25°C):  $\delta$  = 13.04 (s, 2H), 12.04 (s, 2H), 10.88 (s, 2H), 7.51–7.36 (m, 14H), 7.18–7.01 (m, 14H), 6.74 (s, 4H), 5.82 (s, 2H), 4.46 (brs, 4H), 4.02–3.85 (m, 32H), 2.42 (brt, 4H), 2.11–1.27 (m, 160H), 1.10 (s, 24H), 1.00 (s, 24H), 0.87 (brt, 18H);  $^{13}\text{C}$  NMR (400 MHz,  $[\text{D}]\text{CHCl}_3$ , 25°C):  $\delta$  = 173.4, 157.1, 154.8, 153.5, 152.8, 151.5, 151.4, 151.3, 151.2, 138.3, 137.2, 133.5, 128.6, 127.9, 127.8, 127.7, 127.0, 126.9, 123.5, 122.8, 122.7, 110, 110.7, 110.1, 109.8, 106.1, 105.3, 74.7, 74.7, 74.4, 74.3, 73.8, 69.3, 43.5, 35.4, 35.3, 35.2, 32.9, 32.2, 32.1, 30.6, 30.0, 29.9, 29.7, 29.6, 29.4, 29.3, 29.2, 27.2, 26.6, 26.4, 22.9, 17.1, 17.0, 14.4, 11.8, 11.7, 11.6; IR (UATR):  $\nu$  = 2957  $\text{cm}^{-1}$  (m), 2922 (s), 2852 (s), 1695 (m), 1656 (m), 1583 (s), 1508 (s), 1465 (m), 1422 (s), 1386 (w), 1340 (m), 1253 (s), 1200 (s), 1115 (s), 1042 (m), 963 (s), 916 (w), 850 (m); MALDI-TOF MS ( $M_n$  = 3062.62)  $m/z$ : 3063.29; elemental analysis calcd (%) for  $\text{C}_{144}\text{H}_{144}\text{N}_{20}\text{O}_{14}$  ( $M_n$  = 3062.62): C 75.9, H 10.1, N 9.7; found: C 75.3, H 10.0, N 9.3.

Received: June 20, 2001 [Z17322]

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## Synthesis of the (+)-C26–C40 Domain of the Azaspiracids by a Novel Double Intramolecular Hetero-Michael Addition Strategy\*\*

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The azaspiracid natural products (AZA 1–5, ) are causative agents of human poisonings associated with the consumption of shellfish that were first recognized in the Netherlands in 1995.<sup>[1]</sup> Originally isolated from the mussel *Mytilus edulis* cultivated in Killary Harbor, Ireland, the azaspiracids have since been detected in a growing range of aquatic organisms and geographical locations. Physiological aspects of azaspiracid poisoning (AZP) are distinct from those of other known shellfish intoxications. These include delayed onset and prolonged duration of acute symptoms, and necrosis of the intestine, thymus, and liver. Hence, the azaspiracids represent an emerging new class of environmental toxins with serious economic and human health consequences. As a result there is an urgent need of authentic samples for continued environmental monitoring.

Structurally, the azaspiracids are complex  $\omega$ -amino acids that contain within their 40-carbon backbone an unprecedented array of polycyclic, spiro-fused ring systems. Among the members of this class reported to date, minor variations in skeletal substitution occur within the C1–C25 domain, but the C26–C40 portion remains constant. The relative stereochemistries within the C6–C25 and C28–C40 domains of the azaspiracids have been assigned, but neither the stereochemical relationship between these two regions, nor the absolute stereochemistry of either has been established. These factors

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[\*\*] This work was supported by the United States National Institute of Environmental Health Sciences (NIEHS; grant number ES10615), NIEH, and by Bristol-Myers Squibb (CJF). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS, NIEH, or BMS. We thank Dr. A. B. Dounay and Dr. G. Florence for critical reading of the manuscript.

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